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LINKAGE ISOMERS: THEIR PREPARATION AND REACTIONS

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CONTENTS

ABBREVIATIONS

bipy = 2,2′-bipyridyl
4-*t*-butylpy = *t*-butylpyridine
diars = *o*-phenylenebisdimethylarsine
dieen = *N*,*N*′-diethylethylenediamine
dien = diethylenetriamine
dmg = dimethylglyoximato (sometimes referred to as DH or dh)
en = ethylenediamine (1,2-diaminoethane)
Et_4dien = *N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine

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$MeEt_4dien$ = 4-methyl-1,1,7,7-tetraethyldiethylenetriamine
Me_2en = *N,N'*-dimethylethylenediamine
MeCN = acetonitrile (methylcyanide)
paphy = pyridine-2-carboxaldehyde-2'-pyridylhydrazone
phen = 1,10-phenanthroline
ptdn = pentane-2,4-dionato (acetylacetone abbrev. acac)
py = pyridine (or py(N))
$(p\text{-tol})_3P$ = tri-*p*-tolylphosphine
$p\text{-tolSO}_2$ = *p*-toluenesulphinato
tripyam = tri(2-pyridyl)amine
tn = trimethylenediamine
$\pi\text{-}C_5H_5$ = π-cyclopentadienyl
C_3H_3SN = isothiazole
C_8H_7SN = 2-methylbenzthiazole
C_8H_7SeN = 2-methylbenzselenazole
$NC\text{—}C_6H_4\text{—3-}CO_2$ = 3-cyanobenzoato (nitrile co-ordinated)
$NC\text{—}C_6H_4\text{—4-}CO_2$ = 4-cyanobenzoato (nitrile co-ordinated)
$O_2C\text{—}C_6H_4\text{—3-CN}$ = 3-cyanobenzoato (carboxylato co-ordinated)
$O_2C\text{—}C_6H_4\text{—4-CN}$ = 4-cyanobenzoato (carboxylato co-ordinated)
NC—4-py(N) = 4-cyanopyridine (nitrile co-ordinated)
(N)py—4-CN = 4-cyanopyridine (pyridine co-ordinated)
O_2C—4-py(N) = 4-pyridine carboxylato (carboxylato co-ordinated)
(N)py—4-CO_2 = 4-pyridine carboxylato (pyridine co-ordinated)
$O{=}CNH_2$—4-py(N) = 4-pyridine carboxamido (O-amido co-ordinated)
(N)py—4-$CONH_2$ = 4-pyridine carboxamido (pyridine co-ordinated)

A. INTRODUCTION

Few synthetic problems in coordination chemistry in the past two decades have continued to fascinate inorganic chemists as has the design and study of linkage isomers. The first review [1] on the subject listed thirty two isomeric pairs of complexes. Since that time, the number of known linkage isomers has tripled. Of the isomeric pairs reported in the former review, only seven ambidentate ligands were involved, with NO_2^-, SCN^-, CN^- and $SeCN^-$ comprising the majority. The ligands used in the synthesis of linkage isomers at the present time include many larger as well as multidentate molecules (or ions).

The emphasis in most of the earlier work in the area has been on the nature of the metal—ligand interaction [2]. Recent interest includes the use of linkage isomers in the elucidation of both redox [3] and substitution [4] reactions between complex ions. These studies are sometimes complicated by rapid isomerisation to the more stable isomer, especially with the small ligands. Thus, synthetic efforts have centred on potential chelating linkage isomers, as well as on ambidentate ligands in which the two potential co-ordinating sites are widely separated.

Our definition of linkage isomerism follows that of Burmeister [1]: the existence of *at least two* complexes differing *only* in the mode of attachment of a multidentate ligand to the metal atom. This definition excludes *single* complexes that contain different bonding modes of the same ligand * as well as complexes which exhibit ligand reversal only (see page 135).

B. FACTORS OF IMPORTANCE IN LINKAGE ISOMERISM

The relative importance of the factors controlling the observation of linkage isomerism is a subject that has attracted much attention in the literature. A description of the synthetic techniques employed and the elucidation of the importance of the various interactions that might be invoked to explain this phenomenon provides an exciting history in itself, full of controversies and conflicting opinions. However, since the precise mix of these factors is probably different for each set of isomers, we will not give a detailed account of them, using specific examples. Instead we present a concise overview of the subject. For an in-depth treatment of these interactions, in the particular case of the important thiocyanate ligand, the reader is referred to the recent comprehensive and illuminating review by Burmeister [11]. In general, the synthesis of linkage isomers requires a delicate balance of the following factors to produce the intermediate situation which is of interest.

(i) Hard-soft acids and bases (HSAB)

Studies involving ambidentate ligands have led to an understanding of some of the factors which result in a preference of one bonding mode over another in a given complex. These results usually have been rationalised successfully in terms of HSAB [13], both for complexes in which only one bonding mode has been observed and for complexes which are linkage isomers, i.e. hard (class a) metals tend to complex through hard centres whereas soft (class b) metals prefer soft centres.

Figure 1 summarises those metals and their oxidation states for which linkage isomers have been found. Although one might have expected to find the greatest number of examples among the borderline metals, Fig. 1 shows that many metals classified as hard or soft are equally good. This serves to emphasise the fact that the overall hardness and softness of both the metal and the ligand must be considered in the experimental design, i.e. the classification of the metals in Fig. 1 may be modified by the nature of the other ligands bonded to the metal. For example, an electron withdrawing group tends to make the metal harder, thus favouring bonding to the hardest ligand

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* We suggest that a new word be coined to describe this phenomenon since to call these complexes 'isomers' implies that they exist in at least two forms having the same molecular formula. These *single* compounds could be called 'geminites' (from the Latin 'gemini' meaning twins which implies 'identical'). Hence, these are complexes containing identical ligands bonded to the metal through different atoms (a situation even rarer than true linkage isomerism) [5—9, 26].

III (h) Cr	0(s) I(s) Mn	0 (s) II(b) III(h) Fe	II (b) III (h) Co	II (b) Ni	I (s) II(b) Cu	II (b) Zn
0 (s) II (b) Mo		III (h) Ru	I(s) III (b) Rh	II(s) Pd	I (s) Ag	II (s) Cd
0 (s) W	0(s) Re		III (b) Ir	0(s) II(s) IV(s) Pt	I (s) Au	II (s) Hg

Fig. 1. Metals involved in linkage isomerism. Oxidation states given in Roman numerals; h = hard, b = borderline, s = soft.

atom site, this type of simple behaviour being exemplified by the complexes [Pd(phen)$(SCN)_2$] * [2] and [Pd(5-NO_2-phen)$(NCS)_2$] * [10]. Similar alterations of electron density at the metal were originally suggested to account for the compounds [Pd$(NH_3)_2(SCN)_2$] * and [Pd$(PEt_3)_2(NCS)_2$] * [14]. It was thought that π-acceptor ligands such as PEt_3 favour bonding through the thiocyanate N by making the metal harder. In this connection, Jǿrgensen [23] has suggested that the formation of $[Co(NH_3)_5NCS]^{2+}$ and $[Co(CN)_5\text{-}SCN]^{3-}$ may be regarded as a "symbiosis" or a flocking together of like ligands.

Pearson [24] has noted that "antisymbiotic" effects are also known and he offers a very elegant explanation based on the *trans* effect or *trans* influence: "two soft ligands in mutual *trans* positions will have a destabilising effect on each other when attached to class b metal atoms". This approach explains why, for example, in Pd(1-diphenylphosphino-3-dimethylaminopropane)(NCS)-(SCN) * [25] the *N*-bonded thiocyanate is *trans* to P and the *S*-bonded thiocyanate is *trans* to N. Thus, a change from S to N bonding for thiocyanate occurs when the thiocyanate ligand binds *trans* to a soft ligand. The foregoing discussion implicitly assumes the absence of steric effects.

(ii) Steric and electronic effects

Steric requirements may influence the bonding mode of ambidentate ligands as in the complexes $[Pd(dien)(SCN)]^+$ * [27] and $[Pd(Et_4dien)NCS]^+$ [28] where the bulky ethyl groups in the latter complex force the thiocyanate to adopt the linear *N*-bonded linkage. If the discussion is limited to fully saturated ligands (as the amine ligands above) where metal—ligand π-bonding is not a complicating factor the effects can be considered to be mainly steric in origin [11].

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* Linkage isomers of these complexes have not been isolated.

Unfortunately, in most cases it has not been found possible to separate steric and electronic effects. Complexes of the type [Pd(ligand)(NCS)(SCN)] * have been prepared with the bidentate ligands $(C_6H_5)_2P(o\text{-}C_6H_4)As(C_6H_5)_2$, $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$, $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$ and $(C_6H_5)_2$-$PCH_2CH_2P(C_6H_5)_2$ [26]. The mode of co-ordination was discussed in terms of both *trans* electronic influences and steric effects. The question of steric versus electronic control has been extensively reviewed and put into the proper perspective by Burmeister [163] for thiocyanate complexes.

In the solid state, the bonding mode may be affected by the nature of the counter-ion but again it is difficult to determine whether the effect is predominantly steric or electronic. For example, the isomerism of $[Pd(Et_4dien)(SCN)]^+$ [12] occurred with NCS^- as counter-ion but with PF_6^- no isomerism was observed. With $[Pd(Et_4dien)NCS][B(C_6H_5)_4]$ isomerism also occurs, apparently to accomodate the packing requirements of $B(C_6H_5)_4^-$. In this case as well, these effects could be caused, or at least influenced, by subtle electronic interactions rather than by genuine steric effects. In fact, the same type of interaction in the solid state may be taking place as in various solvents (vide infra).

An interesting example where both packing and electronic effects may be important is furnished by the cation-induced linkage isomerisation of $[Co(CN)_5SCN]^{3-}$ [29]. Both linkage isomers were isolated as the potassium salts and it was found that $K_3[Co(CN)_5NCS]$ isomerises to the more stable $K_3[Co(CN)_5SCN]$. When the cation is the tetra-*n*-butylammonium ion the complex $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5SCN]$ is only prepared with difficulty and it isomerises to the *N*-bonded complex.

(iii) Solvent effects

The first observation that the solvent could affect the mode or bonding of an ambidentate ligand was made by Farona and Wojcicki [30] using the complex $Mn(CO)_5SCN$. These investigators found that the thiocyanate was bonded through the *N*-atom in acetonitrile whereas an equilibrium between *N*- and *S*-bonding existed in dichloromethane, 1,2-dichloroethane, chloroform and ethyl acetate. These, and other similar observations [31,32] led to a systematic investigation of the role of the solvent in controlling the bonding mode of co-ordinated thiocyanate, mainly by Burmeister and his co-workers [17,33] and also by Norbury [16,34] and Marzilli [35] and their co-workers. It appears that solvent effects are generally observed when both linkage isomers can be prepared implying that the solvent exerts a small perturbation. This result is predicted by Klopman's treatment of chemical reactivity using the concept of charge- and frontier-controlled reactions [19]. Solvents with high dielectric constants tend to enhance frontier orbital-controlled (covalent) interactions whereas those with low dielectric constants favour charge-controlled (ionic) interactions. These effects are not well-understood and the available data (for

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* Linkage isomers of this complex have not been isolated. See also footnote on p. 111.

square planar complexes with thiocyanate) indicate that soft metals coordinate to the *S*-atom in solvents of high dielectric constant and to the *N*-atom in solvents of low dielectric constant. Hard metals appear to show the opposite solvent effect in coordinating to the *N*-atom in solvents of high dielectric constant and to the *S*-atom in solvents of low dielectric constant.

An example of this opposite behaviour [36] is afforded by the octahedral system

$$(4\text{-}t\text{-butylpy})\mathrm{Co(dmg)_2SCN} \rightleftharpoons (4\text{-}t\text{-butylpy})\mathrm{Co(dmg)_2NCS}$$

For this system the equilibrium lies to the right in aprotic solvents of high dielectric constant and to the left in solvents of low dielectric constant. Since Klopman's ideas predict the same trends for both hard and soft metal centres it has been suggested that the above behaviour results from a modification of the overall softness or hardness of the metal complex by the solvent [36]. Then these results would be in line with those found for square planar complexes. That hydrogen-bonding effects may be important as well is shown by the fact that the sulphur-bonded isomer is favoured in protic solvents of high dielectric constant. Finally, it should be mentioned that the steric differences between octahedral and square planar complexes may also contribute to the effect.

(iv) Kinetic effects

When designing a strategy for the synthesis of linkage isomers, it is important to realise that kinetic factors can often determine which isomer is produced. The thermodynamically unstable isomer, produced by manipulation of kinetic parameters, frequently isomerises to the more stable form.

Kinetically controlled synthetic techniques included in the chemists' bag of tricks are variations in the inner- or outer-coordination spheres [12,28], changes in oxidation state (see pages 117, 135) [162,164], different temperatures [21], and the employment of totally different synthetic routes (see page 137) [22].

C. THEORETICAL CONSIDERATIONS

It is probably premature to say that there is a theoretical basis for explaining linkage isomerism. However, a number of attempts have been made to identify the important interactions involved. Besides the unifying (and non-theoretical) approach of HSAB, a molecular orbital approach [20] and Klopman's ideas [19] seem to provide, at the moment, the most promising semi-empirical methods for explaining this phenomenon.

Using Klopman's development, Norbury [18] has calculated softness parameters for the thiocyanate ligand, taking into account the two highest occupied orbitals with σ-symmetry, σ_3 and σ_4. The parameters obtained are shown in Table 1. These results indicate that when the metal environment is of a borderline nature, it will prefer to bond to an atom of intermediate softness charac-

TABLE 1

Softness character of nitrogen and sulphur in thiocyanate orbitals

	σ_3(N)	σ_3(S)	σ_4(S)	σ_4(N)
Softness (eV)	−14.41	−13.68	−11.66	−10.84

ter, or in this case, the sulphur atom of σ_3 or σ_4. The calculations show that the nitrogen atom of σ_3 is the hardest site available but that the nitrogen atom of σ_4 is the softest site. Thus the idea of symbiosis [23] is justified. It is somewhat surprising that these calculations are consistent with the chemistry of thiocyanate coordination since the π-orbitals have been neglected and these orbitals appear to dominate the metal—sulphur bond properties for the thiocyanato isomers (vide infra). It is interesting to speculate whether a similar calculation on the cyanate ion would give grossly different results for oxygen versus nitrogen bonding since this ion prefers to co-ordinate via the nitrogen atom [37] in almost all cases. This ion should provide a better model for Klopman's equations since π-bonding is unlikely to make an important contribution to the bonding in either isomer.

The problem of involvement of π-bonding in thiocyanate co-ordination has been considered by Gutterman and Gray [20] who have shown that the sulphur atom of thiocyanate can function as a π-donor as well as a σ-acceptor. Burmeister [11] has pointed out that M—SCN bond angles observed in thiocyanato complexes are consistent with involvement of the filled π_2 orbitals on thiocyanate. It would seem worthwhile then to incorporate the molecular orbital results within the framework of Klopman's development in order to test the validity of Norbury's conclusions.

D. PREPARATION OF RECENTLY REPORTED LINKAGE ISOMERS

A summary of papers published on linkage isomerism since Burmeister's review in 1968 [1] up to the end of 1975 is presented in this section.

(i) Simple ligands

(a) Thiocyanato—isothiocyanato. The first example of a metal-catalysed linkage isomerisation of a metal complex which does not proceed by an electron transfer mechanism was reported by Orhanovic and Sutin in 1968 [40]. The mercury(II) ion which catalysed the aquation of $(OH_2)_5CrSCN^{2+}$ was assumed to attack at the sulphur atom of the complex to give $(OH_2)_5Cr(NCS)Hg^{2+}$ and $HgSCN^+$ along with $(OH_2)_6Cr^{3+}$ as final products. The Hg(II) catalysed aquation of the linkage isomer $(OH_2)_5CrNCS^{2+}$ was also studied [41]. In this case, Hg(II) associates with the remote S-atom and no isomerisation is observed. A further example of proposed linkage isomerism ac-

TABLE 2

Linkage isomers of thiocyanate

Linkage isomer	Reference	Linkage isomer	Reference
$[Cr(OH_2)_5(NCS)]^{2+}$	38, 39, 40	$[(NH_3)_5Ir(NCS)]^{2+}$	60, 61
$[Cr(OH_2)_4(NCS)(NCS)]^{+}$	43	*trans*-$[Ir(H)(pip)_4(NCS)]^{+}$	167
$Mo(C_5H_5)(CO)_3(NCS)$	32	$[Ni(diars)_2(NCS)]^{2+}$	62
$Mn(CO)_5(NCS)$	30	$Pd(AsPh_3)_2(NCS)_2$	2, 17, 63—65
$Fe(C_5H_5)(CO)_2(NCS)$	32, 44	$Pd(bipy)_2(NCS)_2$	2, 63, 64
$Fe(CN)_5SCN^{3-}$	164	$Pd(As(n\text{-}C_4H_9)_3)_2(NCS)_2$	66
$[Ru(NH_3)_5(NCS)]^{2+}$	45	$[Pd(Et_4dien)(NCS)]^{+}$	4, 12, 28, 67, 68
$[Co(CN)_5(NCS)]^{3-}$	15, 20, 29, 46	$Pd(4,7\text{-diphenylphen})(NCS)_2$	10
$[Co(NH_3)_5(NCS)]^{2+}$	47, 48, 49, 50, 141	$Pd(P(OCH_3)_3)_2(NCS)_2$	69
$Co(SO_3)(NH_3)_4(NCS)$	51	$[Pd(MeEt_4dien)(NCS)]^{+}$	70
$(NH_3)_5Co(NCS)Co(CN)_5$	52	$[Pt_2Cl_2(PPr_3)_2(SCN)_2]$	168
trans-$[Co(en)_2(NH_3)(NCS)]^{2+}$	53	α-$[Pt_2Cl_2(P(n\text{-}C_3H_7)_3)_2(NCS)_2]$	71
trans-$[Co(ptdn)_2(py)(NCS)]$	54	*trans*-$[(Ph_3P)_2PtH(NCS)]$	72, 74, 75
$Co(dmg)_2(NCS)_2$	165	*trans*-$[(Ph_2EtP)_2PtH(NCS)]$	72, 74, 75
$Co(dmg)_2(py)(NCS)$	34, 35, 55, 56	*trans*-$[(Bu_3P)_2PtH(NCS)]$	72, 74, 75
$Co(dmg)_2(4\text{-}t\text{-butylpy})(NCS)$	35	*trans*-$[(Et_3P)_2PtH(NCS)]$	72—76
$Co(dmg)_2(4\text{-cyanopyridine})(NCS)$	57	*trans*-$[(Et_3As)_2PtH(NCS)]$	72—76
$Co(dmg)_2(4\text{-}NH_2py)(NCS)$	57	*trans*-$[((p\text{-tol})_3P)_3PtH(NCS)]$	72, 75
$Co(dmg)_2(Ph_3P)(NCS)$	57	*cis*-$[Pt(PPh_3)_2(NCS)_2]$	77
$Co(dmg)_2(n\text{-}BuPh_2P)(NCS)$	57	*cis*-$[Pt(AsPh_3)_2(NCS)_2]$	77
$Co(dmg)_2(MePh_2P)(NCS)$	57	*cis*-$[Pt((t\text{-}Bu)C{\equiv}CPPh_2)_2(NCS)_2]$	78
$Co(dmg)_2(n\text{-}Bu_3P)(NCS)$	57	*cis*-$[Pt(PhC{\equiv}CPPh_2)_2(NCS)_2]$	78
$Co(dmg)_2((PhO)_3P)(NCS)$	57	*cis*-$[Pt(EtC{\equiv}CPPh_2)_2(NCS)_2]$	78
$Co(dmg)_2(EtC(CH_2O)_3P)(NCS)$	57	*cis*-$[Pt(i\text{-}Pr)C{\equiv}CPPh_2)_2(NCS)_2]$	78
$Co(dmg)_2((MeO)_3P)(NCS)$	57	$Pt(SMe_2)_2(NCS)_2$	169
$Co(dmg)_2((i\text{-}PrO)_3P)(NCS)$	57	$Cu(tripyam)(NCS)_2$	79, 170
$Co(dmg)_2(aniline)(NCS)$	16	$Cu(dppa)(NCS)_2$	170
$[MeCo(dmg)_2(NCS)]^{-}$	58		
mer-$[Rh(NCS)Cl_2(PMe_2Ph)_3]$	166	$Au[P(OPh)_3](NCS)$	171
$[(NH_3)_5Rh(NCS)]^{2+}$	59, 60	$Au(PMe_3)(NCS)$	171
		$Au(PPh_3)(NCS)$	171
		$[Cd(NCS)_4]^{2-}$	80—82

companying dinuclear complex formation is found in the Hg(II)-catalysed aquation of $(OH_2)_5CrCN^{2+}$ in which the product was postulated to be $(OH_2)_5$-$Cr{-}NC{-}Hg^{4+}$ [42].

In another study, the reaction of $FeSCN^{2+}$ and chromium(II) in the presence of added thiocyanate yielded at least one new set of linkage isomers [43],

$$(OH_2)_5Fe(NCS)^{2+} + Cr(OH_2)_6^{2+} + NCS^- \xrightarrow[0^\circ C]{0.1\ M\ H^+} Cr(OH_2)_6^{3+} + (OH_2)_5CrNCS^{2+}$$
$$+ (OH_2)_5CrSCN^{2+} + (OH_2)_4Cr(NCS)(NCS)^+ + (OH_2)_4Cr(SCN)(NCS)^+$$

It was shown that the $(OH_2)_4Cr(NCS)_2^+$ gave a nearly statistical distribution between the geometric *cis* and *trans* isomeric forms. If the $(OH_2)_4Cr(SCN)$-$(NCS)^+$ product, which was too unstable to allow an isomer separation to be performed, also existed in *cis* and *trans* forms, then there resulted two new sets of linkage isomers: the *cis*-$Cr(OH_2)_4(NCS)_2^+$ and *cis*-$Cr(OH_2)_4(SCN)(NCS)^+$ complexes comprising one set and the *trans*-$Cr(OH_2)_4(NCS)_2^+$ and *trans*-$Cr(OH_2)_4(SCN)(NCS)^+$ compounds comprising the other set. Because it is not certain whether the *cis*- or *trans*-$Cr(OH_2)_4(SCN)(NCS)^+$ complex (or a mixture of both forms) was obtained from the reaction, only one set of isomers is listed in Table 2 with the geometric configuration unspecified.

The possibility of linkage isomerism has been mentioned for the complex $Fe(CN)_5SCN^{3-}$ [164]. Oxidation of the $Fe(CN)_5NCS^{4-}$ (for which the mode of co-ordination was not definitely established) by an excess of $Fe(CN)_6^{3-}$ rapidly produced a transient purple species which changed to the blue colour characteristic of the species obtained directly from $Fe(CN)_5NH_3^{2-}$ and SCN^-. A possible explanation which was suggested for these observations was that the rapid oxidation of the $Fe(CN)_5NCS^{4-}$ complex gave an unstable, purple, *N*-bonded $Fe(CN)_5NCS^{3-}$ ion which slowly rearranged to the blue linkage isomer $Fe(CN)_5SCN^{3-}$.

A general route to the synthesis of complexes of the type $(\pi\text{-}C_5H_5)Fe(CO)_2X$ provided an alternative preparative method to the known thiocyanate linkage isomers of this species [44]. It was found that one mole of bis(π-cyclopentadienyldicarbonyliron) reacts with excess anhydrous ferric perchlorate according to the reaction $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2\,Fe^{3+} \rightarrow 2(\pi\text{-}C_5H_5)Fe(CO)_2S +$ $2\,Fe^{2+}$ where S = a molecule of solvent. If the oxidation is carried out in acetone or methanol, the weakly bound solvent molecule may be easily displaced by SCN^- (and a variety of other ligands) to give the complexes $(\pi\text{-}C_5H_5)$-$Fe(CO)_2NCS$ and $(\pi\text{-}C_5H_5)Fe(CO)_2SCN$ which had previously been made by other methods [32].

The three halopentaammines $[Ru(NH_3)_5X]^{2+}$ (X = Cl, Br, I) were found to react with thiocyanate in aqueous solution at elevated temperature [45]. In each reaction, the halogen was displaced by NCS^- and the formation of $[Ru(NH_3)_5SCN]^{2+}$ resulted. Thermal conversion of this complex as the perchlorate salt to the corresponding *N*-bonded linkage isomer was observed upon heating in DMSO at 70° C for 70 h under a nitrogen atmosphere but only a

10% yield of $[Ru(NH_3)_5NCS]^{2+}$ was obtained.

The first set of cobalt thiocyanate linkage isomers was reported in 1968 [46], although one of the isomers had been synthesised previously [15]. It was found that the substitution of water in $Co(CN)_5OH_2^{2-}$ by SCN^- yields, as the primary product, the nitrogen-bonded isomer,

$$Co(CN)_5OH_2^{2-} + SCN^- \rightarrow Co(CN)_5NCS^{3-} + H_2O$$

whereas the reduction of $Co(NH_3)_5NCS^{2+}$ by $Co(CN)_5^{3-}$ yields, as the primary product, the sulphur-bonded isomer [15].

$$Co(NH_3)_5NCS^{2+} + Co(CN)_5^{3-} \rightarrow Co(CN)_5SCN^{3-} + Co^{2+} + 5\,NH_3$$

The *S*-bonded form of the complex is the stable one as evidenced by the fact that the solid-state isomerisation of $K_3[Co(CN)_5NCS]$ to $K_3[Co(CN)_5\text{-}SCN]$ was found to occur upon heating for 6 h at 150° C or upon allowing a sample of the *N*-bonded form to stand for 3—4 months at room temperature [46]. This isomerisation was found to be strongly influenced by the choice of counterion since the tendency of the tetra-n-butyl-ammonium salt to isomerise in the solid state is reversed, with the *N*-bonded isomer being the stable one, i.e. if a sample of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5SCN]$ is allowed to stand at room temperature, it isomerises to the *N*-bonded form within 3 d [29]. To explain the role that the counterion plays in the isomerisation, it was suggested that the stabilisation of the *N*-bonded isomer was due to an electronic effect in which the polarisable sulphur end of the —NCS is better accommodated by the non-polar, hydrocarbon environment of the $(n\text{-}C_4H_9)_4N^+$ counterion. The stabilisation of the *S*-bonded form of the complex containing K^+ as counterion was attributed to its favourable interaction with the hard end of coordinated —SCN. A more recent study of this system [187] and the analogous one with —SeCN prompted an alternative argument based on the size of the cation. The bonding of NCS^- to the $[Co(III)(CN)_5]$ unit has been investigated by infrared and electronic spectroscopy and a molecular orbital description of the system was constructed [20].

The linkage isomers of thiocyanatopentaamminecobalt(III) were prepared in 1970 [47] to complete the triad of this series, the analogous rhodium and iridium complexes having been reported in 1965 [59—61]. The *N*-bonded form is the stable isomer since the *S*-bonded complex was found to isomerise upon heating in dilute acid or in the solid state. The X-ray crystal structures of both isomers as their chloride salts have been determined [48]. Tracer experiments in the solid state revealed that an important path in the thermal solid state isomerisation involved a dissociation of the originally co-ordinated thiocyanate group [49]. This result showed the inadequacy of the generally made assumption that isomerisation in the solid state is an intramolecular process, and contrasted with the mechanism in aqueous solution in which isomerisation occurred without exchange with $N^{14}CS^-$ in solution [47]. The photochemical isomerisation of $Co(NH_3)_5SCN^{2+}$ to the *N*-bonded isomer in solution and in the solid state has also been studied [50].

Recently, the labilising effect of a *trans* ligand has been used to promote linkage isomerisation in a Co—SCN system [51]. The conversion of $Co(SO_3)(NCS)(NH_3)_4$ to $Co(SO_3)(SCN)(NH_3)_4$ was reported to be favoured by the *trans* effect of the sulphito group. The brown complex $Co(SO_3)(NCS)(NH_3)_4 \cdot 2\,H_2O$ formed from aqueous solution contained *N*-bonded thiocyanate. Upon dehydration, the red complex $Co(SO_3)(SCN)(NH_3)_4$ containing *S*-bonded thiocyanate was formed.

A number of other studies involving new sets of cobalt—thiocyanate linkage isomers have been described. The binuclear complexes $(NH_3)_5Co(NCS)Co(CN)_5$ and $(NH_3)_5Co(SCN)Co(CN)_5$ reported in 1972 [52] represent the first example of complexes containing linkage isomers of a single SCN in a bridging position. In the same year [53] the syntheses of *trans*-$[en_2NH_3CoSCN]^{2+}$ and *trans*-$[en_2NH_3CoNCS]^{2+}$ were reported along with a detailed base hydrolysis study of the *S*-bonded isomer. Also, the linkage isomerisation of thiocyanatopyridinebis(2,4-pentanedionato)cobalt(III) was observed to occur upon sitting in chloroform

$$trans\text{-}[Co(ptdn)_2(SCN)(py)] \xrightarrow{CHCl_3} trans\text{-}[Co(ptdn)_2(NCS)(py)]$$

The isomerisation was found to proceed in the solid state at 68°C with $t_{1/2} \approx$ 12 h [54].

An unusual system in which all three possible linkage isomers were prepared was reported in 1973 for tetraphenylarsonium *trans*-(dithiocyanato)bis(dimethylglyoximato)cobaltate(III) [165]. All isomers, $[Co(dmg)_2(SCN)_2]^-$, $[Co(dmg)_2(SCN)(NCS)]^-$ and $[Co(dmg)_2(NCS)_2]^-$ were extensively studied by PMR and infrared spectroscopy.

Burmeister et al. [17] have reported that the bonding mode of co-ordinated thiocyanate ion in solution was dependent upon the nature of the solvent, Pd—SCN bonding being promoted by solvents having high dielectric constants. However, Norbury et al. [34] studied the complex *trans*-$[Co(dmg)_2py(NCS)]$ and its linkage isomer and observed Co—NCS bond formation in solvents of high dielectric constant. On the basis of these studies, the latter workers concluded that solvents of high dielectric constant favour *S*-bonding in linkage isomers of class b metals but *N*-bonding in linkage isomers of class a metals. Hassel and Burmeister [56] re-investigated this system and reported that the conclusions reached by Norbury et al. were erroneous. They proposed that when the complex *trans*-$Co(dmg)_2(py)(SCN)$ was dissolved in high or low dielectric solvents, the different bonding modes exhibited were kinetically rather than thermodynamically controlled so that the effect of solvent was obliterated. The S→N bonded isomerisation was proposed to proceed via a dissociative or ion-pair mechanism since in solvents with high dielectric constants, the rate of isomerisation was relatively rapid.

Epps and Marzilli [35] then studied this sytem again and the analogous one in which L = 4-t-butylpyridine. They found that the linkage isomerisation underwent cobalt(II) catalysed equilibration in solvents with a high dielectric constant. Since cobalt(II) was present in catalytic amounts even in analytically pure samples, they postulated that the equilibration was cobalt(II) catalysed and was not an ionic process as Hassel and Burmeister had proposed. These results strongly supported the theories advanced by Norbury and co-workers.

Other complexes of the type *trans*-$LCo(dmg)_2SCN$ which were found to exhibit linkage isomerisation were those for which L = amine, phosphine or phosphite ligands [57]. The S : N equilibrium constants in nitrobenzene were determined. These reactions are examples of a new class of ligand exchange reactions which proceed only in the presence of catalytic amounts of $LCo(II)(dmg)_2$. In separate studies the analogous complexes $Co(dmg)_2$(aniline)(NCS) [16] and $[MeCo(dmg)_2(NCS)]^-$ [58] and their linkage isomers were also reported.

In 1967, it was found that the *mer*-$[Rh(NCS)Cl_2(PMe_2Ph)_3]$ complex upon heating, gives an isomer which was thought to be the linkage isomer *mer*-$[Rh(SCN)Cl_2(PMe_2Ph)_3]$ [166]. The infrared spectra of both isomers were consistent with this assignment although the M—SCN range was obscured by bands due to the PMe_2Ph ligands. The $\nu(C{\equiv}N)$ frequencies of the two isomers in chloroform were virtually identical.

The existence of $HIr(piperidine)_4(NCS)_2$ as a mixture of *N*- and *S*-bonded thiocyanate linkage isomers was inferred from NMR spectra [167], since a two-peaked hydride resonance was observed in d^6-DMSO and methanol solutions.

The only example of nickel—thiocyanate linkage isomers was described by Preer and Gray [62] for the complex $[Ni(diars)_2NCS]^{2+}$. They obtained infrared spectral evidence that both the *N*- and *S*-bonded thiocyanate complexes co-existed at equilibrium in acetonitrile, dichloromethane and DMSO at room temperature but no experimental details were given.

Studies on palladium linkage isomers have been continued. The $[Pd(MeEt_4dien)(SCN)]^+$ complex was found to isomerise completely in solution to the *N*-bonded isomer and to reisomerise in the solid state with tetraphenylborate as counterion, in a completely analogous fashion to the $[Pd(Et_4dien)(SCN)]^+$ complex [70].

$$[Pd(MeEt_4dien)(SCN)][B(C_6H_5)_4] \underset{\text{solid state}}{\overset{\text{solution}}{\rightleftharpoons}} [Pd(MeEt_4dien)(NCS)][B(C_6H_5)_4]$$

A study of the lanthanide-induced shifts in thiocyanate complexes employed the linkage isomers of $(\pi\text{-}C_5H_5)Fe(CO)_2(NCS)$ and $Pd(AsPh_3)_2(NCS)_2$ [65]. It was found that the *N*-bonded thiocyanates experience only a very small shift whereas *S*-bonded thiocyanates, with a terminal nitrogen available for co-ordination with the lanthanide, experience a significant shift. Thus, a convenient method is available for distinguishing between linkage isomers of the thiocyanate group as long as the compounds contain some protons. It was suggested that the method could be used to supplement the sometimes ambiguous infrared evidence that is widely used to assign the bonding in these isomers.

Although the first example of thiocyanate linkage isomers involving platinum was reported in 1961 [71], more than a decade passed before any further examples were discovered. Now, however, more than a dozen sets are known. Linkage isomerism in complexes of the general type *trans*-[L_2-PtH(SCN)] and *trans*-[L_2PtH(NCS)] is exhibited for L = Bu_3P, Et_3P, $EtPh_2P$, Ph_3P, Et_3As and (p-tol)$_3$P [72,73]. The NMR spectra of solutions of these complexes show two triplets, the higher set significantly broadened. Powell and Shaw [73] attributed this broadening to interaction between the hydridic proton and the quadrupolar ^{14}N nucleus. These broadened lines were reasonably assigned to the Pt—N isomer whereas the sharp triplet corresponded to the Pt—S complex. On the basis of studies of the effects on the spectra of adding phosphines and changing the temperature, Adlard and Socrates [74,75] stated that this method of assignment of specific isomers is not acceptable, claiming that ligand exchange appears to be responsible for the broadening. However, Pidcock [76] has shown that ligand exchange does not account for this broadening and has re-affirmed the original interpretation of Powell and Shaw.

Adlard and Socrates [72] used absorbances of the Pt—D stretching bands in the infrared spectrum to calculate NCS/SCN isomer ratios which compared favourably with the results calculated from NMR intensity ratios. The effect of steric crowding was also discussed. In chloroform, *N*-bonding was favoured and was dependent on the nature of the tertiary phosphine or arsine in the complex, increasing in the order

$$Et_3P \sim Bu_3P < Et_3As < Ph_2EtP < Ph_3P < (p\text{-tol})_3P$$

Two solid state isomerisation reactions were found during an investigation of the systems *cis*-[Pt(PPh_3)$_2$(SCN)$_2$] and *cis*-[Pt($AsPh_3$)$_2$(SCN)$_2$] [77]. Both underwent exclusively *cis* *S*-bonded → *cis* *N*-bonded isomerisations in the solid phase upon heating. A number of thiocyanato platinum acetylenic derivatives *cis*-[Pt(NCS)(SCN)($Ph_2PC{\equiv}CR$)] and *cis*-[Pt(NCS)$_2$($Ph_2PC{\equiv}CR$)] where R = Ph, Et, i-Pr and t-Bu were synthesised recently and were isolated in the solid state [78]. Mixtures of both *S*- and *N*-bonded isomers were found in various solvents and the effect of solvent was discussed.

The use of $^1H\{^{195}Pt\}$ INDOR spectroscopy revealed the presence in dichloromethane solution of the three isomers [Pt(SCN)$_2$(SMe_2)$_2$], [Pt(SCN)(NCS)(SMe_2)$_2$] and [Pt(NCS)$_2$(SMe_2)$_2$] in the approximate proportions 1 : 0.7 : 0.2 [169]. In view of the sometimes ambiguous assignments of bonding mode based on infrared spectroscopy, it seems likely that various NMR studies will become more popular in the future.

Complexes having two ambidentate ligands may potentially be isolated in three linkage isomeric forms and with the preparation of the Cu(dppa)-(NCS)$_2$ complexes [170] the number of cases in which all three isomers have been obtained for the thiocyanate ligand rises to three (the others being Co(dmg)$_2$(NCS)$_2$ and Cu(tripyam)(NCS)$_2$). The isomers Cu(dppa)(NCS)$_2$, Cu(dppa)(SCN)(NCS) and Cu(dppa)(SCN)$_2$ were characterised mainly by infrared, electronic and diffuse reflectance spectroscopy.

Linkage isomers of *trans*-dithiocyanatoaurate(III) were reported in 1971 by Negoiu and Baloiu [83] as both the potassium and tetraethylammonium salts. However, Melpolder and Burmeister [84] later disputed this work and suggested that the so-called *N*-bonded isomer was really the ionic thiocyanato complex, $[Au(CN)_2(H_2O)_2](SCN)$. Since the characterisation of this complex by the earlier workers was apparently in error, these 'isomers' are not included in Table 2.

Genuine thiocyanate linkage isomers of gold have apparently been detected by infrared spectroscopy in 1,2-dichloroethane solution for AuL(SCN) complexes (L = $P(OPh)_3$, PMe_3 and PPh_3) although the *N*-bonded isomer was a very minor component in all of the solutions [171]. It was concluded that the proportion of the *N*-bonded isomer present increased as the *trans*-influence of the L ligand increased, completely in accordance with Pearson's antisymbiotic *trans*-influence principle.

The effect of solvent on the linkage isomers of $[Cd(NCS)_4]^{2-}$ was reported in 1972 [82]. The complex $Cs_2[Cd(SCN)_4] \cdot H_2O$ exhibits Cd—SCN bonding in aqueous solution and in the solid state but isomerises in methanol to give Cd—NCS bonding. The change from an *S*-bond in aqueous solution to an *N*-bond in methanol was rationalised in terms of the lesser polarity of the latter solvent. Evidently, in a less polar solvent, cadmium tends towards a more polar bonding with the nitrogen atom of the NCS^- group.

(b) Selenocyanato—isoselenocyanato. Although the literature is replete with examples of thiocyanate linkage isomers, few sets of selenocyanate isomers are known (Table 3). This appears to be the result of the relative insensitivity of the metal—selenocyanate bonding mode to the nature of other ligands in the first co-ordination sphere. The observation [85] that metal—thiocyanate attachment was sensitive to the oxidation state of the metal and to the degree of replacement of CO with ligands of lesser π-bonding capacity suggested that selenocyanato metal carbonyl linkage isomers might be made by controlling these factors. Using these ideas, the linkage isomers $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)_2(SeCN)$ and $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)_2$-(NCSe) were made by reacting $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)_2(PhCH_2)$ with

TABLE 3

Linkage isomers of selenocyanate

Linkage isomer	Reference
$Fe(C_5H_5)(CO)(PPh_3)_2(NCSe)$	85
$[Ru(NH_3)_5(NCSe)]^{2+}$	45
$[Pd(Et_4dien)(NCSe)]^+$	4, 9, 68, 86—88
$Pd(P(n\text{-}C_4H_9)_3)_2(NCSe)_2$	69
$[Co(CN)_5NCSe]^{3-}$	187, 188

$Se(SeCN)_2$ [85]. Both compounds were stable with respect to interconversion at room temperature. At higher temperatures, deselenation to $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)_2(CN)$ takes place in preference to isomerisation.

The only known examples of ruthenium—selenocyanate linkage isomers are the $[Ru(NH_3)_5(SeCN)]^{2+}$ and $[Ru(NH_3)_5(NCSe)]^{2+}$ complexes reported in 1971 [45], although it is not clear from the paper how the latter complex was prepared. Molar conductance measurements were made on the *N*-bonded isomer only and electronic spectra were reported for the *Se*-bonded isomer only.

The first observation of the influence of the nature of a non-co-ordinated group on the bonding modes of an ambidentate ligand was reported for $[Pd(Et_4dien)SeCN][B(C_6H_5)_4]$ [86]. This complex was shown to undergo *Se*→*N*-bonded isomerisation in a variety of solvents [4,87]. However, once isolated in the solid state, the *N*-bonded isomer re-isomerises to the *Se*-bonded form. It was suggested that, in forming the crystal, the steric interaction of the selenium atoms with the non-co-ordinated tetraphenylborate ions is more important than their interaction with the ethyl groups of the co-ordinated amine [86]. A far-infrared spectral study showed that the N→Se isomerisation went nearly to completion at 40°C with a half-life of 1.6 d (as compared to 2.2 d for the analogous thiocyanate complex) [68]. The solid state isomerisation of the other known palladium—selenocyanate complex known to exhibit linkage isomerism, $[Pd(P(n\text{-}C_4H_9)_3)_2(SeCN)_2]$ was observed to occur upon heating [69]. The ability of this complex to form both isomers, *Se*- and *N*-bonded, was thought to be the result of the steric requirements of the tri-n-butylphosphine ligands.

The complex $[Co(CN)_5NCSe]^{3+}$ was prepared by Gutterman and Gray [20] as both the potassium and tetra-n-butylammonium salts. These investigators mentioned the possibility that the *Se*-bonded isomer was present in significant amounts as the potassium salt, whereas the $[(n\text{-}C_4H_9)_4N]^+$ salt was completely *N*-bonded. Pure samples of the *Se*-bonded isomer were prepared later by Melpolder and Burmeister [187] employing the following synthetic routes

$$[Co(NH_3)_5NCSe]^{2+} + [Co(CN)_5]^{3-} + 6\,H_2O \rightarrow [Co(CN)_5SeCN]^{3-}$$
$$+ [Co(OH_2)_6]^{2+} + 5\,NH_3$$

and

$$Co(NCSe)_4Hg + 5\,KCN \rightarrow K_3[Co(CN)_5SeCN] + 2\,KSeCN + \tfrac{1}{2}\,Hg_2(SeCN)_2$$

The equilibrium distribution of the two linkage isomers in a variety of solvents was measured by infrared spectroscopy. The isomerisation was thought to involve a dissociative process $[Co(CN)_5SeCN]^{3-} \rightarrow [Co(CN)_5]^{2-} + NCSe \rightarrow [Co(CN)_5NCSe]^{3-}$ since in all of the solvents, except those in which dissociation is complete (acetonitrile and DMSO) an initial increase in the ionic SeCN absorption, followed by a decrease, was observed. Similar results were obtained for the corresponding thiocyanate linkage isomers.

An interesting observation resulting from the solvent studies was that in all of the aprotic solvents used, $[Co(CN)_5SCN]^{3-}$ always isomerised or dissociated faster than $[Co(CN)_5SeCN]^{3-}$. The opposite behaviour is predicted using only hard/soft arguments (parameters), since the softer selenium atom of selenocyanate would be expected to form a weaker bond than the sulphur of thiocyanate. It was concluded that the intrinsic strength parameters, which are usually ignored, assume greater importance for hard/soft or soft/hard interactions, such as those encountered here, and these are no longer swamped by the hard or soft parameters.

(c) Cyano—isocyano. The reactions of Cr^{2+} with $Co(NH_3)_5CN^{2+}$, *trans*-$Co(NH_3)_4(H_2O)CN^{2+}$ and *trans*-$Co(en)_2(H_2O)(CN)^{2+}$ have been studied [89]. A metastable intermediate, formulated as $(H_2O)_5CrNC^{2+}$ was postulated to be common to all three reductions. It isomerised quantitatively to $(H_2O)_5$-$CrCN^{2+}$ under all conditions. Evidence has also been presented that the reaction of $CrCN^{2+}$ with Hg^{2+} is accompanied by internal ligand isomerisation and that the cation complex is $Cr—NC—Hg^{4+}$ [42,172].

Cyanide linkage isomerism has been found to occur in the solid state for the polymeric complex of approximate composition $Fe_3[Cr(CN)_6]_2$. The combination of infrared spectroscopy, X-ray powder diffraction, magnetic susceptibilities and Fe^{57} Mössbauer spectroscopy indicates that four distinct structures occur at different stages in the isomerisation of this solid. The initial face-centred cubic material contains $Fe^{2+}—N{\equiv}C—Cr^{3+}$ linkages and has interstitial Fe^{2+} ions. In the first reaction step the interstitial Fe^{2+} displaces Cr^{3+} from the carbon octahedra to give a half-isomerised complex with both Fe^{2+} and Cr^{3+} in the carbon octahedra and Cr^{3+} in interstitial sites. In the presence of air, this complex undergoes further rearrangement and partial oxidation. The oxidised compound can then be reduced to give the true linkage isomer, that is, the complex containing $Cr^{3+}—N{\equiv}C—Fe^{2+}$ linkages with Fe^{2+} in interstitial sites [91].

A similar Co—Cr system was also studied which involved a clear case of linkage isomerism. A compound of approximate composition $Co_3[Cr(CN)_6]_2$

TABLE 4

Linkage isomers of cyanide

Linkage isomer	Reference
$[Cr(OH_2)_5CN]^{2+}$	42, 89, 90, 172
$K[Fe(II)(CN)_6Cr(III)]$	93
$Fe_3[Cr(CN)_6]_2$	91
$Co_3[Cr(CN)_6]_2$	92
$[Co(CN)_5CN]^{3-}$	94, 95
cis-α-$[Co(trien)(CN)_2]^+$	96
$(NH_3)_5CoCNCo(CN)_5$	173—175

was found, in the absence of air, to undergo a complete linkage isomerisation [92] as illustrated by

$Co^{2+}(NC)_6Cr(III) \xrightarrow{\Delta} Cr^{3+}(NC)_6Co(II)$

An interesting pair of linkage isomers employing a cyanide bridge between two metal centres has been prepared. It was found [173] that the dehydration of $[Co(NH_3)_5OH_2][Co(CN)_6]$ proceeds in part, according to

$$[Co(NH_3)_5OH_2][Co(CN)_6] \rightarrow [(NH_3)_5CoNCCo(CN)_5] + H_2O \qquad (1)$$

Conductivity and molecular weight measurements were consistent with this formulation as was the ion-exchange behaviour on cation- and anion-exchange resins. Infrared measurements in the 2100—2000 cm^{-1} region provided strong evidence for the presence of a cyanide bridge in the binuclear complex and the electronic spectrum corresponded to that expected for the sum of the spectra of the $Co(CN)_6^{3-}$ and $(NH_3)_5CoNC^{2+}$ moieties. It was concluded from base-catalysed aquation studies that there was no scrambling of ammonia and cyanide ligands around the two cobalt(III) centres. Although the evidence favoured the formulation of the complex as $[(NH_3)_5NCCo(CN)_5]$, the possibility of its being the linkage isomer in which the orientation of the bridging cyano group is reversed, could not be definitely ruled out. Accordingly, a crystal structure determination was carried out [174] which verified the original assignment given in eqn. (1). The preparation of the linkage isomers was, however, reported in a subsequent publication [175]. The synthetic method employed cleverly exploited the relative ease of substitution of water in $Co(CN)_5OH_2^{2-}$ and the nucleophilicity of the nitrogen end of cyanide in $Co(NH_3)_5CN^{2+}$.

$$Co(NH_3)_5CN^{2+} + Co(CN)_5OH_2^{2-} \rightarrow (NH_3)_5CoCNCo(CN)_5 + H_2O$$

Again the bonding mode in the two isomers was assigned on the basis of the electronic spectrum and the same physical measurements were carried out on this complex as on the previously prepared isomer [173]. The base hydrolysis reaction of $(NH_3)_5CoCNCo(CN)_5$ was found to be considerably slower than that of its linkage isomer.

(d) Cyanato—isocyanato. In general, O-bonded cyanates in inorganic systems are rare and are characterised with difficulty. The first (and only known) example of solid linkage isomers containing *N*- and *O*-bonded cyanate groups are the compounds $Rh(PPh_3)_3NCO$ (yellow) and $Rh(PPh_3)_3OCN$ (orange) which were reported in 1974 [97]. The authors noted that the mode of coordination of the cyanate group depended upon the nature of the solvent, i.e. treatment of $Rh(PPh_3)_3Cl$ with Ph_4AsNCO in MeCN yields the *N*-bonded isomer whereas the addition of EtOH to the reaction mixture results in formation of the cyanate form. Both compounds dissolved in $CHCl_3$ gave identical solutions with ν_{CN} at 2235 cm^{-1} and similarly in benzene both had ν_{CN} at 2227 cm^{-1}.

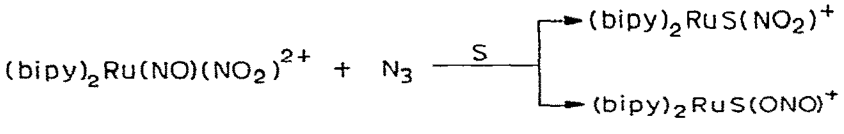
TABLE 5

Linkage isomers of nitrite

Linkage isomer	Reference
$[Ru(bipy)_2(OH_2)NO_2]^+$	176
$[Ru(bipy)_2(HOCH_3)NO_2]^+$	176
$[Ru(bipy)_2(OC(CH_3)_2)NO_2]^+$	176
$[Ru(bipy)_2(NCCH_3)NO_2]^+$	176
$[Ru(bipy)_2(py)NO_2]^+$	176
$Ru(bipy)_2I(NO_2)$	176
$Ru(bipy)_2Cl(NO_2)$	176
$[Co(NH_3)_5NO_2]^{2+}$	98—108
$[Co(en)_2(NO_2)_2]^+$	109—111
$[Co(NH_3)_2(py)_2(NO_2)_2]^+$	109
$[Co(CN)_5NO_2]^{3-}$	94
cis-$[Co(tn)_2(NO_2)_2]^+$	161
$[Rh(NH_3)_5NO_2]^{2+}$	59, 112, 113
$[Ir(NH_3)_5NO_2]^{2+}$	112, 113
$Ni(Me_2en)_2(NO_2)_2$	31, 114
$Ni(dieen)_2(NO_2)_2$	31
$Ni(en)_2(NO_2)_2$	114
$[Ni(NO_2)_4(NO_2)_2]^{4-}$	115
$[Pt(NH_3)_4(NH_2)(NO_2)]^{2+}$	113, 179

An earlier report that a set of platinum—cyanate linkage isomers had been prepared was subsequently disclaimed. Powell and Shaw [73] reported that the *trans*-$[PtH(OCN)(PEt_3)_2]$ complex showed three broad absorptions in the NMR spectrum due to the isocyanato complex and a smaller triplet which was assigned to the *O*-bonded species. Adlard and Socrates [74] later disputed the existence of the cyanato complex, claiming that the smaller triplet was due to an impurity present in the former study.

(e) Nitro—nitrito. It was found that mixtures of nitro—nitrito isomers resulted from the reaction of $(bipy)_2Ru(NO)(NO_2)^{2+}$ with solvent molecules according to



where S = H_2O, CH_3OH or $(CH_3)_2CO$ [176].

Furthermore, displacement of the weakly bound acetone molecule in the resulting $(bipy)_2Ru(OC(CH_3)_2)(NO_2)^+$ complex by added L where L = CH_3CN, OH_2 or py gives $(bipy)_2RuL(NO_2)^+$ and $(bipy)_2RuL(ONO)^+$ mixtures. When L = I^- or Cl^- the uncharged species $(bipy)_2RuL(NO_2)$ and $(bipy)_2RuL$-

(ONO) result. The nitrito isomers were converted to the more stable nitro isomers only by prolonged heating either in solution or in the solid state. The exceptions to this observation are the acetone and methanol complexes $(bipy)_2RuS(NO_2)^+$ and $(bipy)_2RuS(ONO)^+$ (S = $(CH_3)_2CO$, CH_3OH) which are labile, providing a path for isomerisation. Each retains a constant nitro to nitrito ratio for several hours in solution, apparently because the isomers are of comparable stability with the nitrito isomer being slightly favoured.

The photochemical behaviour of $[(NH_3)_5CoNO_2]^{2+}$ has been investigated in solution and in the solid state [105—108]. In solution, it was found that oxidation—reduction decomposition involving the NO_2^- ligand and nitro→ nitrito linkage isomerisation occur simultaneously. Irradiation of a solid sample of $[(NH_3)_5CoNO_2](NO_3)_2$ in a nujol mull converted the compound almost completely into the nitrito isomer [105]. In another photochemical study of this compound, an intermediate thought to involve bidentate chelate attachment of the nitrite ligand was postulated [106]. The activation energies and ΔH value for this process were determined by differential thermal analysis (DTA) and differential scanning calorimetry (DSC) [177]. The values obtained closely agreed with those obtained earlier [103]. A significant result of this work was the clear indication that the nitrito—nitro isomerisation is exothermic whereas the nitro—nitrito conversion is endothermic.

Linkage isomers of another cobalt—nitrite complex employing the chelating ligand trimethylenediamine have been observed. The electronic and infrared spectra for *cis*-$[CoNO_2(ONO)tn_2](NO_2)$ and *cis*-$[Co(NO_2)_2tn_2](NO_2)$ were reported along with the preparative procedures for making both isomers [161]. One other study was done on nitro—nitrito linkage isomers of the Co triad. The visible and UV absorption spectra of $[Rh(NH_3)_5NO_2]^{2+}$ and $[(NH_3)_5\text{-}Rh(ONO)]^{2+}$ were recorded and the observed ligand field bands were interpreted by the usual theoretical procedures [59].

The infrared spectrum of $Ni[2\text{-(aminomethyl)pyridine}]_2(NO_2)_2$ was suggestive of the presence of both nitro and nitrito linkages [178], but the electronic spectrum gave evidence only of the nitrito group. No isomerisation was observed in solution. Since the possibility of linkage isomerism in this system is still open to question, this example has not been included in Table 5.

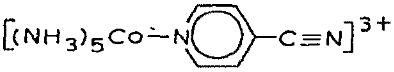
The $[Ni(en)_2(NO_2)_2]$ and $[Ni(en)_2(ONO)_2]$ complexes have been prepared. The known stable red dinitro compound was converted into the blue dinitrito isomer upon heating, with the transition temperature being at 74 ± 2°C [114]. It was also noted that the pink colour of bis(*N,N'*-dimethylethylenediamine)-dinitronickel(II) turns to mauve (characteristic of the dinitrito isomer) at 140°C but returns to pink on cooling. Similarly, a solution of bis[*N*-ethylethylenediamine]dinitronickel(II) in *o*-dichlorobenzene is pink but becomes dark blue (characteristic of the dinitrito isomer) at 150°C [114]. This last set of isomers was not, however, sufficiently characterised to warrant its inclusion in Table 5 at this time.

The reported isolation of linkage isomers of $[(NH_3)_5Pt(NO_2)]^{3+}$ [113] has been challenged by Sabbatini and Balzani [179]. On the basis of elemental analyses, conductivity measurements and titration data, they concluded that the nitro complex was such a strong acid that it could not exist in aqueous solution but could only be obtained as the amido complex $[(NH_3)_4Pt(NH_2)(NO_2)]^{2+}$. The nitrito complex, on the other hand, existed as the expected $[(NH_3)_5Pt(ONO)]^{3+}$ between pH 4—9. Below pH 4, isomerisation and decomposition reactions occur. Since it is probable that the nitrito complex exists as $[(NH_3)_4Pt(NH_2)(ONO)]^{2+}$ above pH 9, then there are linkage isomers of the amido species. Table 5 lists the complex as the tetraammine as opposed to the pentaammine in light of the above remarks.

(ii) Large ligands

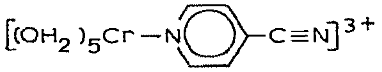
One of the most fascinating developments in the study of linkage isomers in the last decade has been the rapid proliferation of compounds containing large ambidentate ligands bound in linkage isomeric forms (Table 6).

Both the pyridine bonded and nitrile bonded isomers of pentaaquochromium(III) have been reported [3]. The chromium(II) reduction of

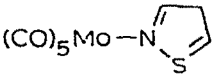


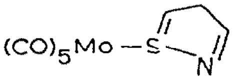
produced initially the chromium(III) compound

which subsequently rearranged in the presence of Cr^{2+} to give its linkage isomer

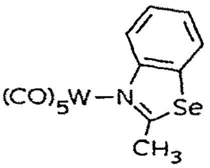


Four interesting sets of isomers employing isothiazole and its derivatives were reported in 1972 [116]. The molybdenum pentacarbonyl of the parent isothiazole was found to bond through either the S or N of the organic ligand.





Linkage isomers of 2-methylbenzselenazole employing W—Se and W—N linkages also were prepared [116].



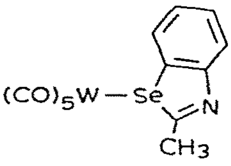
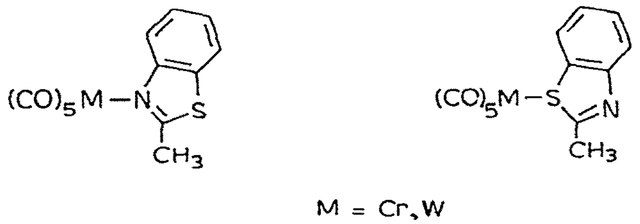


TABLE 6

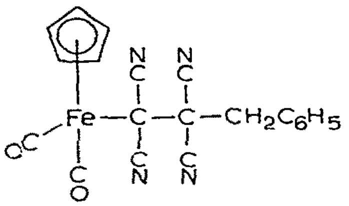
Linkage isomers of large ligands

Linkage isomer	Reference
$[Cr(OH_2)_5(\text{4-cyanopyridine})]^{3+}$	3
$Cr(CO)_5(C_8H_7SN)$	116
$Cr(C_5H_5)(NO)_2C(CN)_2C(CN)_2CH_2Ph$	117
$Mo(C_5H_5)(CO)_3SO_2CH_2Ph$	118, 119
$Mo(CO)_5(C_3H_3SN)$	116
$W(CO)_5(C_8H_7SeN)$	116
$W(CO)_5(C_8H_7SN)$	116
$Mn(CO)_5SO_2CH_2Ph$	118, 119
$Mn(CO)_5SO_2CH_3$	118
$Re(CO)_5SO_2CH_3$	118
$Fe(bipy)_2p\text{-tolSO}_2$	120—122
$Fe(C_5H_5)(CO)_2SO_2CH_2Ph$	118
$Fe(C_5H_5)(CO)_2SO_2CH_3$	118
$[Ru(NH_3)_5NH_2CH_2COO]^{2+}$	162
$[Ru(NH_3)_5(\text{4-cyanobenzoate})]^{2+}$	123
$Co(bipy)_2p\text{-tolSO}_2$	121, 122
$[Co(NH_3)_5(\text{4-cyanopyridine})]^{3+}$	3, 125
$[Co(NH_3)_5(\text{3-cyanobenzoate})]^{2+}$	128
$[Co(NH_3)_5(\text{4-cyanobenzoate})]^{2+}$	128
$[Co(NH_3)_5(\text{3-pyridinecarboxylate})]^{2+}$	156, 157
$[Co(NH_3)_5(\text{4-pyridinecarboxylate})]^{2+}$	156, 157
$[Co(NH_3)_5(NH_2CHO)]^{3+}$	129
$Ni(bipy)_2p\text{-tolSO}_2$	121, 122
$Zn(bipy)_2p\text{-tolSO}_2$	131
$Hg(C_6H_5)(SO_2C_6H_5)$	181—184
$Hg(C_2H_5)(SO_2C_2H_5)$	183, 184

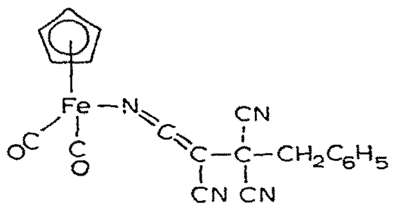
Similarly, complexes of 2-methylbenzthiazole which exhibited linkage isomerism were synthesised as chromiumpentacarbonyl and tungstenpentacarbonyl derivatives [116].



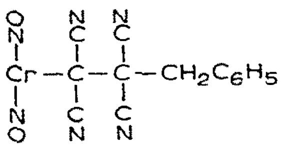
Studies on tetracyanoethylene insertion reactions have provided some novel examples of linkage isomers. The reaction between $C_5H_5Fe(CO)_2CH_2C_6H_5$ and tetracyanoethylene in dichloromethane yielded two products which were readily separable by alumina chromatography [180]. On the basis of chemical analyses, molecular weight measurements and infrared spectroscopy, they were assigned the following structures.



and

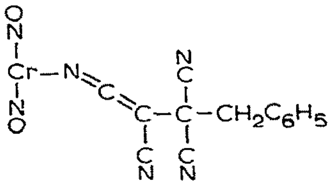


The insertion of tetracyanoethylene into the Cr—$CH_2C_6H_5$ bond of (π-C_5H_5)Cr(NO)$_2$$CH_2C_6H_5$ complex also yielded two linkage isomeric products [117].



(I)

and

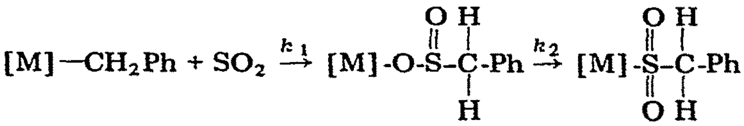


(II)

Both isomers were isolated as solids and there was infrared evidence that isomer I was slowly converted into isomer II in CH_2Cl_2.

The anions of sulphinic acids have proven to be a fruitful source of linkage isomers in the last few years. Low-valent transition metals generally show preference for the more polarisable donor atom of an ambidentate ligand. Therefore, most of the sulphinato complexes isolated from the reaction between metal alkyls and sulphur dioxide exhibit metal—sulphur bonding [118]. However, it was found that reactions of transition metal alkyls and aryls of the type (π-C_5H_5)Fe(CO)$_2$$CH_2C_6H_5$, Mn(CO)$_5$$CH_2$Ph, Mn(CO)$_5$$CH_3$, ($\pi$-$C_5H_5$)Fe(CO)$_2$$CH_3$, ($\pi$-$C_5H_5$)Mo(CO)$_3$$CH_2C_6H_5$ and Re(CO)$_5$$CH_3$ in liquid SO_2 or in organic solvents containing SO_2 proceed by the intermediacy of the oxygen-bonded sulphinates which subsequently rearrange to the thermodynamically stable and isolable sulphur-bonded sulphinates [118]. The *O*-sulphinato complexes were reasonably stable in the presence of sulphur dioxide, with the stability being highest when R = CH_3, but complete removal of SO_2 caused immediate isomerisation to the corresponding *S*-sulphinates.

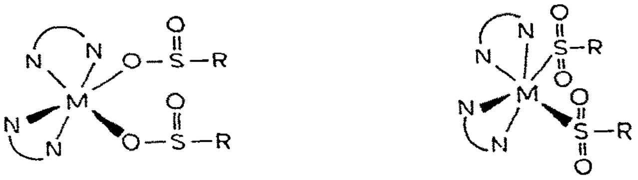
In an NMR study of the sulphur dioxide insertion reaction with the compounds (π-C_5H_5)Fe(CO)$_2$$CH_2$Ph, ($\pi$-$C_5H_5$)Mo(CO)$_3$$CH_2$Ph and Mn(CO)$_5$-$CH_2$Ph, a two-step mechanism in which the *O*-bonded sulphinate was formed first, followed by linkage isomerism to the *S*-bonded species, was again postulated [119].



$$[M]{-}CH_2Ph + SO_2 \xrightarrow{k_1} [M]\text{-}O\text{-}\overset{\overset{O}{\|}}{S}\text{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}\text{-}Ph \xrightarrow{k_2} [M]\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}\text{-}Ph$$

$[M] = (\pi\text{-}C_5H_5)Fe(CO)_2, (\pi\text{-}C_5H_5)Mo(CO)_3, Mn(CO)_5$.

A number of linkage isomers of the type $M(bipy)_2(p\text{-}tolSO_2)$ in which the sulphinate ion is bound to the metal either by the sulphur or one of the oxygens, have been prepared recently as well (M = Fe(II) [120—122], Co(II) [121,122], Ni(II) [121,122] and Zn(II) [131]).

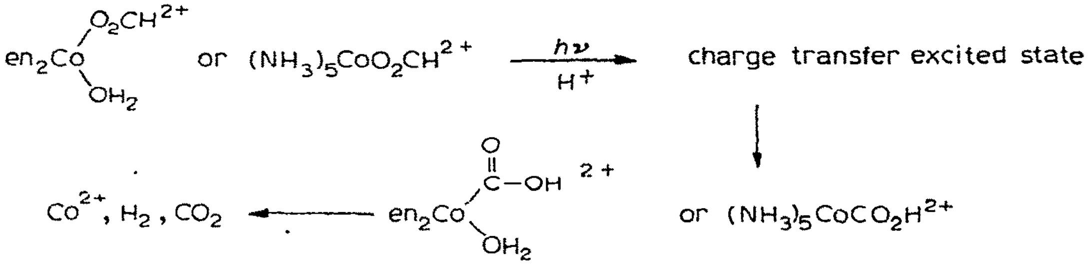


R = *p*-toluene

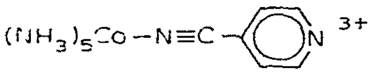
The Mössbauer, infrared and electronic spectra of the compounds were examined and their magnetic moments were measured. It was concluded that the *S*-bonded ion had a considerably larger ligand field strength than the *O*-bonded sulphinate ion [121].

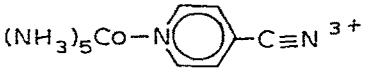
Interaction of $Hg(C_6H_5)_2$ or $Hg(C_2H_5)_2$ with liquid SO_2 was found to give almost quantitative yields of the corresponding monosulphinates. The phenylsulphinate, $(C_6H_5SO_2)Hg(C_6H_5)$ was isolated in two linkage isomeric forms, which are *S*- and *O*-bonded [181—184]. The latter arose from the former upon crystallisation. The ethylsulphinate, $(C_2H_5SO_2)Hg(C_2H_5)$ is *S*-bonded in the solid state but adopts a monomeric *O*-bonded structure in solution [183]. The X-ray powder diffraction patterns were different for each isomer and the infrared spectra provided additional evidence for the assignments [184]. Isomers of $p\text{-}MeC_6H_4Hg(SO_2Ph)$ have not been isolated but when a sample was allowed to sit for several weeks, it was found to be a mixture of two different crystalline forms, one of which was identical to the freshly prepared compound. These two forms were considered to be linkage isomers [184] but since other explanations are possible, this species is not included in Table 6 at this time.

An intriguing case involving two examples of proposed O→C "linkage" isomerism for the formate ligand have been reported [124]. These do not constitute true linkage isomers by our definition since the isomerism is accompanied by proton migration, i.e. the proton is attached to the oxygen in the *C*-bonded complex and to the carbon in the *O*-bonded complex. This is an example of structural isomerism only.



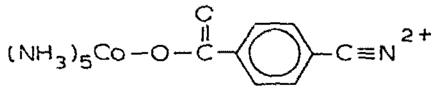
The preparations of the linkage isomers of (4-cyanopyridine)pentaamminecobalt(III) in which the cobalt is bound through the nitrile nitrogen in III and through the pyridine nitrogen in IV, have been described recently [3,125].

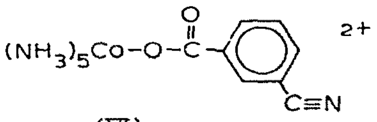

(III)


(IV)

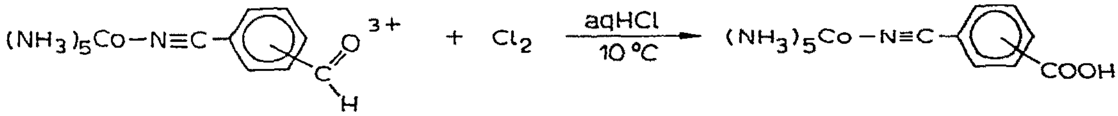
The analogous linkage isomers of this ligand with Ru(II) may have been made but the characterisation was not conclusive and these isomers have not been included in Table 6 [126].

Isomeric pairs of pentaamminecobalt(III) compounds with 3- and 4-cyanobenzoate have been prepared using totally different synthetic routes. Complexes V and VI in which the cobalt is bonded to the carboxylate oxygens were first prepared by standard procedures in 1961 [127].

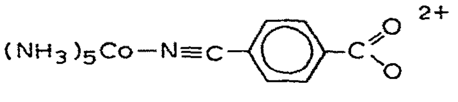

(V)


(VI)

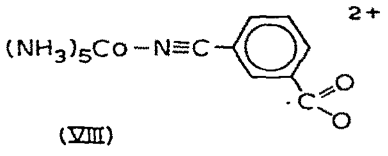
The linkage isomers of these species, in which the cobalt is bonded to the nitrile nitrogen, were recently prepared [128] by oxidising the corresponding nitrile-bonded (3-cyanobenzaldehyde)pentaamminecobalt(III) and (4-cyanobenzaldehyde)pentaamminecobalt(III) complexes with Cl_2 according to



The complexes were isolated in the solid state as the 3+ species [128] but there was good evidence that the carboxylic acid group became deprotonated in solution: (i) there was a change in the UV—visible spectrum upon adding H^+ to an aqueous solution of these complexes; (ii) there was an inverse $[H^+]$ term in the Cr^{2+} reduction studies of the 4-cyanobenzoic acid complex (isomer VII) and (iii) the isomers VII and VIII moved down an ion-exchange column at pH 7 faster than a 3+ ion which indicated that the compounds had a charge of 2+. Thus, the linkage isomers of V and VI were formulated as VII and VIII respectively.

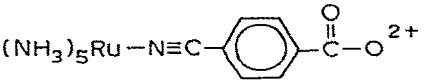


(VII)



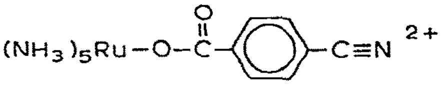
(VIII)

The analogous set of isomers of ruthenium(III) with 4-cyanobenzoic acid (IX and X) have also been made [123],



(IX)

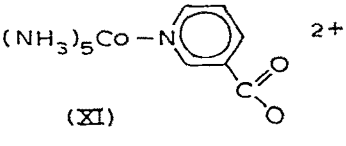
and



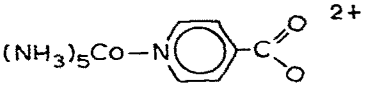
(X)

The reaction of $(NH_3)_5Ru(OH_2)^{2+}$ with 4-cyanobenzoic acid gave exclusively the cyano co-ordinated Ru(II) complex whose UV—visible spectrum indicated that the species existed in both acid and base forms. Oxidation of this compound gave the ruthenium(III) isomer IX, which had a pH-sensitive UV—visible spectrum indicative of a free carboxyl group. The carboxylate co-ordinated linkage isomer, X, on the other hand, was formed directly from the ruthenium(III) complex $[(NH_3)_5Ru(OH)][S_2O_6]$ by reacting it with 4-cyanobenzoic acid in an aqueous slurry. Thus, the different pathways leading to the formation of 4-cyanobenzoatopentaammineruthenium(III) linkage isomers are a nice illustration of the basic differences in specificity of the reactions of the Ru(II) and Ru(III) pentaammines.

The 3- and 4-pyridinecarboxylic acid (nicotinic and isonicotinic acid, respectively) complexes with pentaamminecobalt(III) were prepared in 1971 [156].

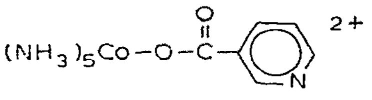


(XI)

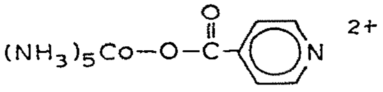


(XII)

The carboxyl groups have dissociable protons and the K_a values for each complex were determined. The above study complements an earlier one [157] in which the carboxylate co-ordinated linkage isomers of XI and XII were prepared.



(XIII)

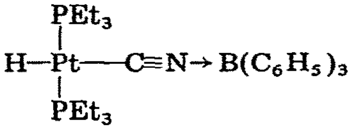


(XIV)

Thus, XI and XIII form one linkage isomeric pair (with 3-pyridinecarboxylate) and XII along with XIV form another pair (with 4-pyridinecarboxylate).

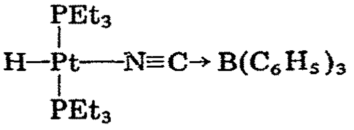
Linkage isomers of formamidopentaamminecobalt(III) have been prepared and the Cr^{2+} reduction studies were performed with the complexes to indicate some of the factors which are important in bridged electron transfer reactions [129] (see page 147).

A new class of compounds of the type *trans*-$HPt(PEt_3)_2CN \rightarrow$ (Lewis acid) were reported to produce linkage isomers (XV and XVI) when the Lewis acid employed was triphenylborane [130].



$$\mathrm{H{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}C{\equiv}N{\rightarrow}B(C_6H_5)_3}$$

XV



$$\mathrm{H{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}N{\equiv}C{\rightarrow}B(C_6H_5)_3}$$

XVI

Assuming that the compounds cannot exist in the absence of the Lewis acid, then the 'ligand' must be considered to be $-C{\equiv}NB(C_6H_5)_3$ in one case and

TABLE 7

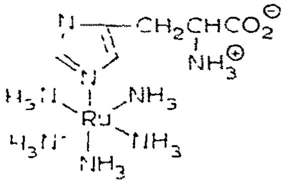
Linkage isomers of chelating ligands

Linkage isomer	Bonding modes	Reference
$[Cr(OH_2)_4$(3-formyl-ptdn)$]^{2+}$	(*O,O*)—(*O,O*)	22
$Cr(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	(*S,S*)—(*O,O*)	133
$Cr(S_2C_2O_2)_3((PPh_3)_2Ag)_3$	(*S,S*)—(*O,O*)	133
$Mo(CO)_4$(paphy)	(*N,N*)—(*N,N*)	134
[Co(cysteine)$_3]^{3-}$	(*S,N*)—(*S,O*)	186
Co(ptdn)$_2$(3-formyl-ptdn)	(*O,O*)—(*O,O*)	135
Co(ptdn)(3-formyl-ptdn)$_2$	(*O,O*)—(*O,O*)	135
[Co(en)$_2$(3-formyl-ptdn)$]^{2+}$	(*O,O*)—(*O,O*)	22
Ni(3-hydroxyimino-4,9-dimethyl-5,8-diazodeca-4,9-diene-2,11-dionato)$_2$	(*N,N*)—(*N,O*)	136
Pt(PPh$_3$)$_2$(benzo-2-carboxaldehyde-2′-pyridylhydrazone)	(*N,S*)—(*N,O*)	138
Cu(2-pyridyl pyrazylmethyl ketone)$_2$	(*N,O*)—(*N,O*)	139

—N≡CB(C_6H_5)$_3$ in the other. These do not, then, give linkage isomers under our definition since the ligands are completely different, one involving a N and B acid—base interaction and the other having a C to B interaction.

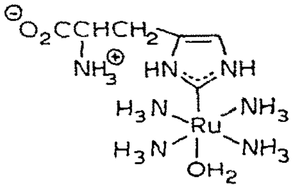
Another example of this kind of 'reversal' involves the complexes $TiCl_4 \cdot NCS(C_2H_5)$ and $TiCl_4 \cdot SCN(C_2H_5)$ [185]. Again, two different ligands were used to prepare the complexes, i.e. ethyl isothiocyanate and ethyl thiocyanate. The carbon on the ethyl group is bonded to sulphur in one complex and to nitrogen in the other. Thus, these do not form linkage isomers under our definition since we require that the isomers can differ only in the mode of attachment of a multidentate ligand to a metal ion.

Synthetic routes leading to complexes of DL-histidine with Ru(II) and Ru(III) in which the histidine exhibits bonding through the carbon and nitrogen atoms of the pyrolle ring have appeared in the literature [132].



(XVII)

(a) Ru (II) (b) Ru (III)



(XVIII)

(a) Ru(II) (b) Ru(III)

However, in going from the *N*-bonded form XVII to the *C*-bonded isomer XVIII one of the amines has evidently been replaced with a water molecule so that these compounds are, strictly speaking, no longer isomers because they do not have the same molecular formula. This is another example of 'ligand reversal' only.

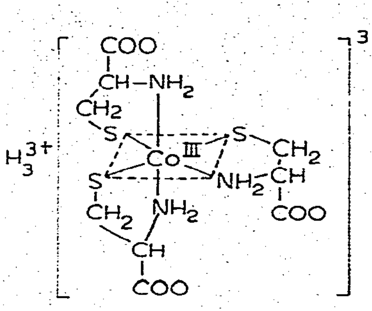
The first ruthenium linkage isomers employing an amino acid as the ambidentate ligand have been reported [162]. The *N*-bonded complex was originally prepared as the Ru(II) complex and this was oxidised with potassium dichromate in acid solution to give the corresponding Ru(III) species. Since Ru(III) has a higher affinity for oxygen than nitrogen, isomerisation occurred with an inverse acid term to give the *O*-bonded linkage isomer which would be rapidly protonated in acidic solution.

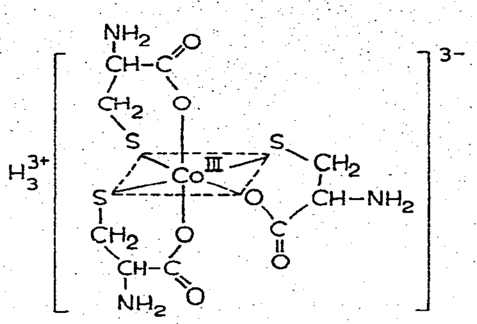
$$\begin{tikzcd}
{[(NH_3)_5Ru(II)NH_2CH_2COOH]^{2+}} \arrow[r, "\text{oxidise}", "H^+"'] & {[(NH_3)_5Ru(III)NH_2CH_2COO]^{2+}} \arrow[d, "\text{isomerise}"] \\
{[(NH_3)_5Ru(III)OOCCH_2NH_3]^{3+}} & {[(NH_3)_5Ru(III)OOCCH_2NH_2]^{2+}} \arrow[l, "H^+", "\text{rapid}"']
\end{tikzcd}$$

The species $[(NH_3)_5Ru(III)NH_2CH_2COOH]^{3+}$ must deprotonate at the carboxyl end for isomerisation to be consistent with the inverse acid term in the rate law so the linkage isomers $[(NH_3)_5Ru(III)NH_2CH_2COO]^{2+}$ and $[(NH_3)_5Ru(III)OOCCH_2NH_2]^{2+}$ must exist.

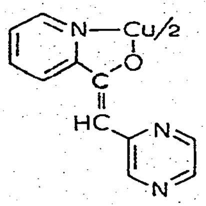
(iii) Chelating ligands

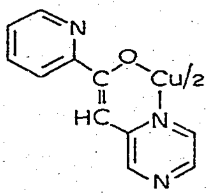
Linkage isomers involving chelated ligands are still comparatively rare (Table 7). The first example of the phenomenon was reported in 1956 with the synthesis of the two forms of tris-cysteinatocobaltate(III) [186].



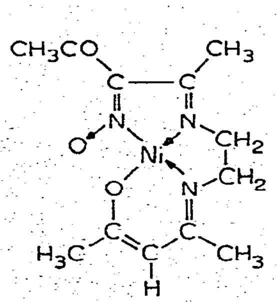


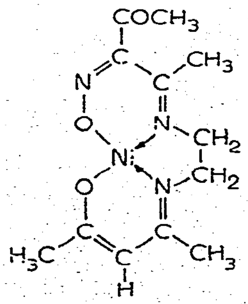
In 1962, it was found that two types of chelates were formed with copper(II) and the ligand 2-pyridyl pyrazylmethyl ketone: (1) chelation with the pyridine nitrogen and the carbonyl oxygen forming a five-membered chelate ring and (2) chelation with the pyrazine nitrogen and the carbonyl oxygen forming a six-membered chelate ring [139].





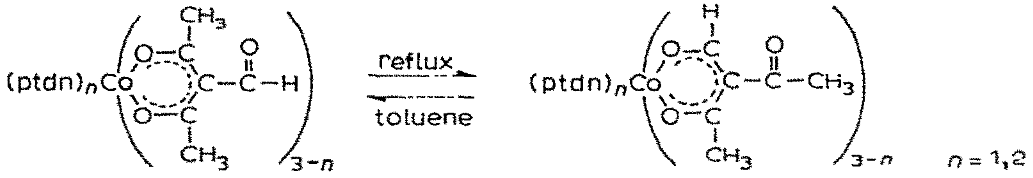
Another pair of chelate linkage isomers were found in the oxime complexes of nickel(II) employing the ligand 3-hydroxyimino-4,9-dimethyl-5,8-diazodeca-4,9-diene-2,11-dione [136].



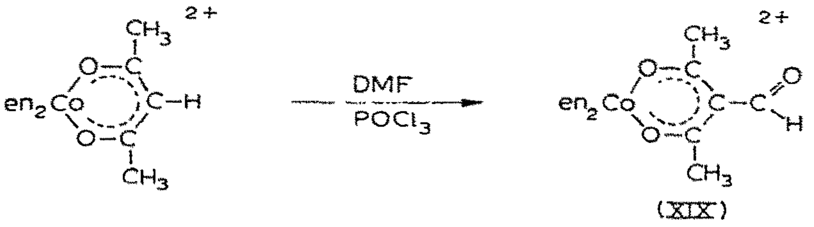


These linkage isomers also involve a change from a five-membered to a six-membered ring system involving the metal atom. Considerable study has shown that the preferred structural configuration of complexes of this type is that in which the metal atom is chelated to both a five- and a six-membered ring simultaneously [137]. However, it was observed that for these Ni(II) linkage isomers, each isomer slowly isomerised to an equilibrium mixture on heating it in solution [136].

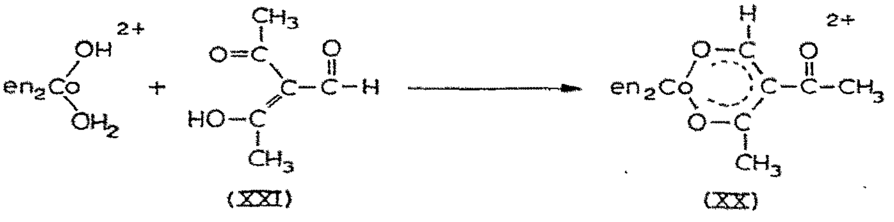
In 1965, Collman and Sun [135] observed that the ligand 3-formylpentane-2,4-dione isomerises to give linkage isomers with Co(III).



The cobalt atom is (*O*,*O*)-bonded in each isomer but different oxygen atoms are involved in each case. Two more pairs of linkage isomers employing this ligand have recently been reported [22]. Unlike the complexes of Collman and Sun, however, the bis(ethylenediamine)cobalt(III) complexes of this ligand, XIX and XX, were found to be stable with respect to isomerisation and were prepared by two different synthetic routes (eqns. 2 and 3).

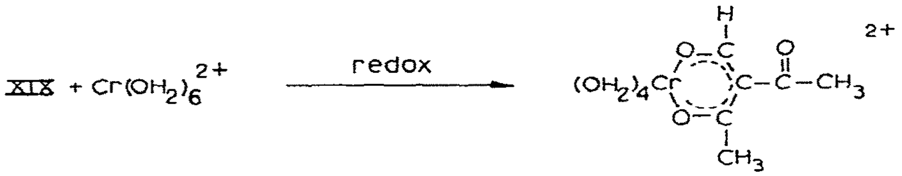


(2)

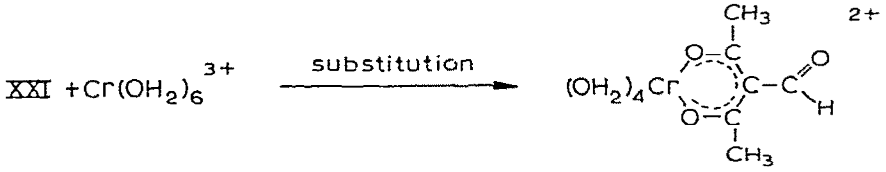


(3)

The tetraaquochromium(III) complexes of this ligand were also prepared. The isomer XXII was obtained as the product of the Cr^{2+} reduction of XIX whereas XXIII was the result of substitution of the free ligand XXI on $Cr(OH_2)_6^{3+}$.

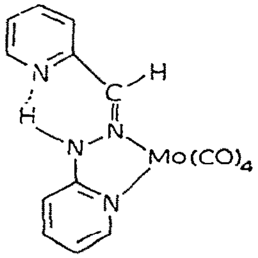


(XXII)

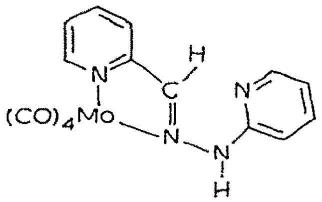


(XXIII)

The ligand, paphy, was found to form linkage isomers with molybdenum(0) in which the metal was (*N*,*N*)-bonded in each isomer but to different nitrogen atoms [134]. The two isomers were prepared by different synthetic routes. Isomer XXIV was prepared by direct reaction of paphy with molybdenum hexacarbonyl in diglyme at 125° C. Isomer XXV resulted from reaction of paphy with the chloropentacarbonylmolybdate(0) anion at room temperature. Compound XXV was relatively unstable in air, giving extensive decomposition within one week.

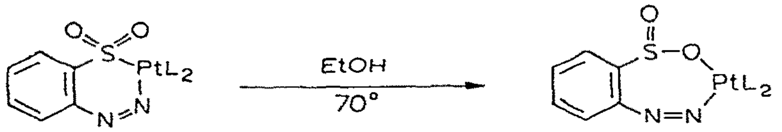


(XXIV)



(XXV)

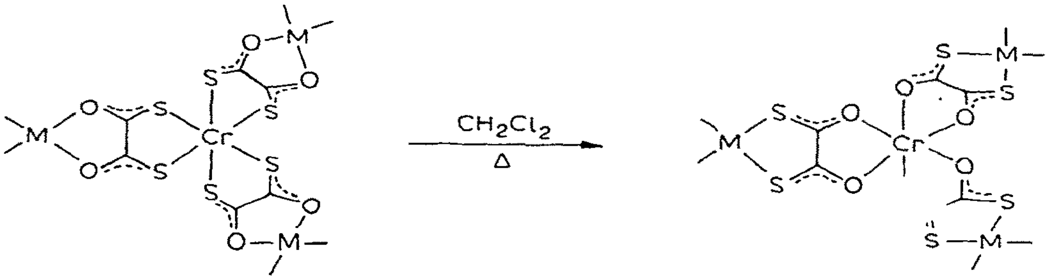
In 1968, Cook and Jauhal [138] reported the *S*- and *O*-bonded linkage isomers of benzo-2-carboxaldehyde-2'-pyridylhydrazone complexes with platinum(0).



L = triphenylphosphine

The thermally stable *S*-bonded isomer was differentiated from the *O*-bonded complex by the position of the OSO antisymmetric stretch in the infrared spectrum.

An interesting set of chelating linkage isomers which also involve (*S*,*O*)-isomerism, have been reported recently for the dithiooxalate dianion [133]. The presence of four donor atoms and the possibilities of charge delocalisation on any two of these atoms makes this a versatile ligand with unique coordination abilities. Properties consistent with Cr—SS or Cr—SO coordination were observed for the $Cr(S_2C_2O_2)_3((PPh_3)_2M)_3$ (M = Cu, Ag) complexes when they were crystallised rapidly from CH_2Cl_2 or benzene solutions. Prolonged standing of these solutions resulted in products for which the infrared spectra showed the appearance of a new C—O absorption near 1380 cm^{-1}. This band reached maximum intensity after refluxing a CH_2Cl_2 solution of the Cr—SS bonded isomers for about 8 h. This was interpreted in terms of a kinetically controlled linkage isomerisation process in which the $Cr—S_2C_2O_2—M$ linkages change to $Cr—O_2C_2S_2—M$ (M = Cu, Ag).



E. LINKAGE ISOMERS GENERATED VIA INNER-SPHERE REDOX REACTIONS

The reduction of complexes containing ambidentate ligands provides a synthetic route to linkage isomers when the inner-sphere [140] mechanism is utilized. Examples are collected in Table 8. The product formed as a result of transfer of the ambidentate ligand to the reductant can be either the thermodynamically stable or unstable isomer often depending on the overall hardness or softness of the reductant. The nature of the product formed may also be dependent upon which linkage isomer is used as oxidant and upon the electronic configuration and stereochemistry of the ambidentate ligand employed. The reduction of the linkage isomers of thiocyanatopentaamminecobalt(III) by chromium(II) shown in Scheme 1 illustrates these points [141].

Reduction of the thermodynamically stable complex $(NH_3)_5CoNCS^{2+}$ leads to the unstable isomer $(OH_2)_5CrSCN^{2+}$. Normally, hard Cr^{2+} prefers to bond to the hard nitrogen atom but the linear Co—NCS linkage forces the reductant to attack at the remote soft sulphur atom. The *S*-bonded

TABLE 8

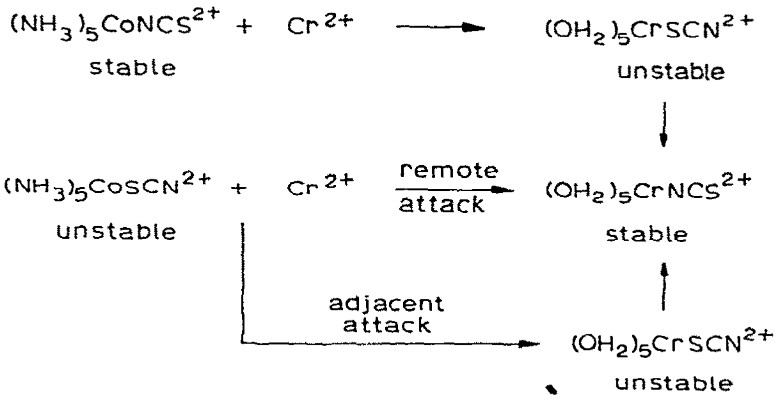
Production of linkage isomers by inner-sphere reduction reactions

Oxidant [a]	Reductant	Product [a]	Reference
(a) Production of the thermodynamically stable isomer			
$(NH_3)_5CoNCS^{2+}$	$Co(CN)_5^{3-}$	$Co(CN)_5SCN^{3-}$	15, 142
$(NH_3)_5CoSCN^{2+}$	$Co(CN)_5^{3-}$	$Co(CN)_5SCN^{3-}$	143
$(NH_3)_5CoNCSe^{2+}$	$Co(CN)_5^{3-}$	$Co(CN)_5SeCN^{3-}$	187
$(NH_3)_5CoNH_2CHO^{3+}$	Cr^{2+}	$Cr(OH_2)_5O{=}CHNH_2^{3+}$	129
$(NH_3)_5Co(4\text{-}CNpy(N))^{3+}$	Cr^{2+}	$Cr(OH_2)_5(N)py{-}4\text{-}CN^{3+}$	3
$(NH_3)_5Co(NC{-}C_6H_4{-}4\text{-}CO_2)^{2+}$	Cr^{2+}	$Cr(OH_2)_5(O_2C{-}C_6H_4{-}4\text{-}CN)^{2+}$	128
$(NH_3)_5Co(NC{-}C_6H_4{-}3\text{-}CO_2)^{2+}$	Cr^{2+}	$Cr(OH_2)_5(O_2C{-}C_6H_4{-}3\text{-}CN)^{2+}$	128

Oxidant [a]	Reductant	Initial product [a,b]	Reference
(b) Production of both linkage isomers of oxidised reductant			
$(NH_3)_5CoNCS^{2+}$	Cr^{2+}	$Cr(OH_2)_5SCN^{2+}$(I)	141
$(NH_3)_5CoSCN^{2+}$	Cr^{2+} [c]	$Cr(OH_2)_5SCN^{2+}$(I,EE)	141
	Cr^{2+} [d]	$Cr(OH_2)_5NCS$ (stable)	141
$Hg(SeCN)_4$	$Co(CN)_5^{3-}$	$Co(CN)_5SeCN^{3-}$ [c] (stable)	20, 187
	$Co(CN)_5^{3-}$	$Co(CN)_5NCSe^{3-}$ [d] (I?)	20, 187
$(NH_3)_5Co((N)py{-}4\text{-}CONH_2)^{3+}$	Cr^{2+}	$Cr(OH_2)_5O{=}CNH_2{-}4\text{-}py(N)^{3+}$(EE)	147
$(NH_3)_5Co(N)py{-}4\text{-}CN)^{3+}$	Cr^{2+}	$Cr(OH_2)_5NC{-}4\text{-}Py(N)^{3+}$(EE)	3
$(NH_3)_5CoCN^{2+}$	Cr^{2+}	$Cr(OH_2)_5NC^{2+}$(I,EE)	148

[a] The first atom of a ligand to be written is the coordinated one. [b] The other isomer is obtained by either isomerisation (I) or electron exchange (EE). [c] Adjacent attack. [d] Remote attack.

SCHEME 1



chromium(III) complex produced in this fashion isomerises to the more stable *N*-bonded form. This is the most commonly used method of generating both linkage isomers. In the case of the chromium(II) reduction of the thermodynamically unstable complex, $(NH_3)_5CoSCN^{2+}$, the bent cobalt—SCN bond allows both adjacent (sulphur) and remote (nitrogen) attack producing both chromium linkage isomers.

In the particular case of the reduction shown in Scheme 2A [15,142], both the oxidant and the product are thermodynamically stable and only one linkage isomer is produced. In Scheme 2B [143] adjacent attack takes place, again forming the stable isomer. The result of Scheme 2, in which the thermodynamically stable product is formed directly, is most commonly observed. However, often Scheme 2B, which features adjacent attack, may be prohibited on steric grounds.

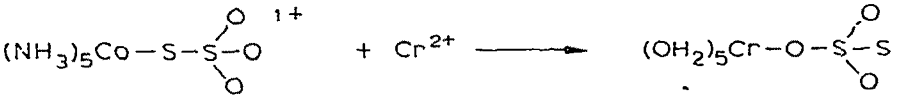
SCHEME 2

$$\underset{\text{stable}}{(NH_3)_5CoNCS^{2+}} + Co(CN)_5^{3-} \longrightarrow \underset{\text{stable}}{(CN)_5CoSCN^{3-}} \qquad \text{A}$$

$$\underset{\text{unstable}}{(NH_3)_5CoSCN^{2+}} + Co(CN)_5^{3-} \longrightarrow \underset{\text{stable}}{(CN)_5CoSCN^{3-}} \qquad \text{B}$$

A further example of Scheme 2A is furnished by the chromium(II) reduction of $(NH_3)_5CoS{-}SO_3^+$ [144] (see eqn. (4)).

Based on the observation of two different reaction rates for the chromium(II) reduction of the thiosulphatopentaamminecobalt(III) complex, Peters and Fraser [145] had previously reported that this complex as usually prepared contains a mixture of *O*- (90%) and *S*-bonded isomers. However, using the same preparative procedures, the product isolated was later found to be sulphur-bonded by X-ray crystallography in the solid state [144,146] and this assignment was supported by PMR studies in solution [144]. In addition, only one rate for chromium(II) reduction [144], which was not in agreement with either of the previously reported values [145], was observed in this later study. The reduction appears to occur exclusively by remote attack with production of a single product [144].

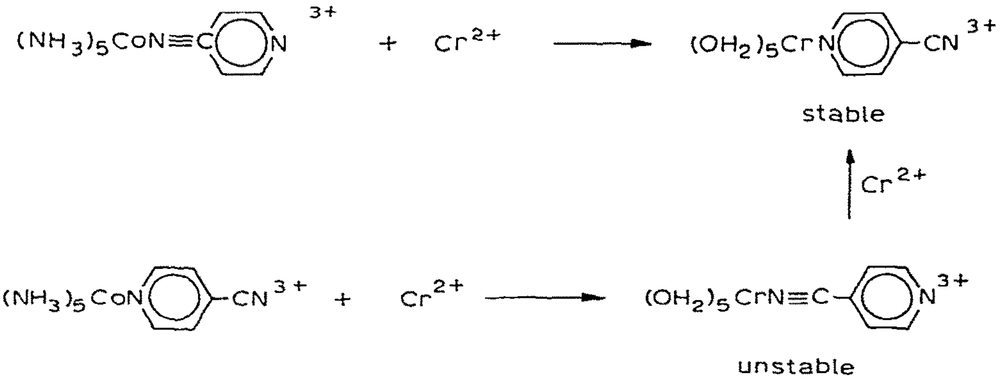


$$(NH_3)_5Co{-}S{-}SO_3^{\,1+} + Cr^{2+} \longrightarrow (OH_2)_5Cr{-}O{-}SO_2{-}S^{\,1+} \qquad (4)$$

Thus, linkage isomers of the thiosulphate ligand are not yet known.

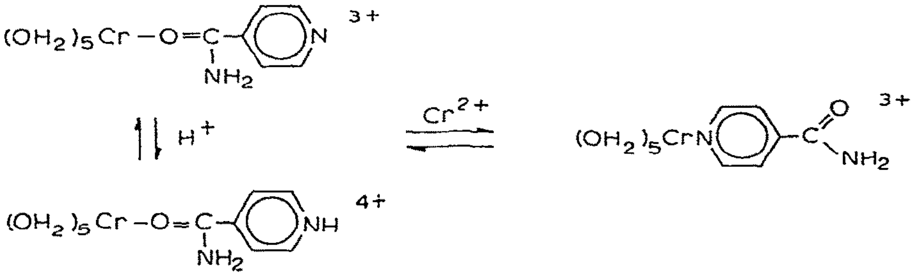
When isomerisation of the initial linkage isomer formed does not or cannot occur, the other isomer is sometimes formed by a second electron transfer. The reduction of the linkage isomers of $(NH_3)_5Co(4\text{-cyanopyridine})^{3+}$ shown in Scheme 3 provides an example of this [3].

SCHEME 3



The chromium(III) nitrile-bonded complex is unstable with respect to aquation but the electron exchange with Cr^{2+} is fast and the stable isomer bonded through the pyridine nitrogen, is produced.

A similar situation occurs in the reduction of 4-pyridinecarboxamidopentaamminecobalt(III) by Cr^{2+} where an equilibrium mixture of the linkage isomers XXVI and XXVII is formed [147].



(XXVI) (XXVII)

The production of XXVII by electron exchange involves an inverse hydrogen ion term thus implying that the deprotonated form of XXVI does exist.

At the very least, an inner-sphere redox reaction may provide a unique synthetic route to the formation of one linkage isomer. A general synthetic path can potentially lead to the formation of the other isomer [22] (see page 138).

F. KINETIC STUDIES

(i) Isomerisation

Most of the kinetic data for linkage isomerisation involves the nitro—nitrito pair. Burmeister has summarised these [1] and a few examples involving SCN→ NCS, NC→ CN and SeCN→ NCSe isomerisations. Table 9 summarises the kinetic studies carried out since the previous review [1].

For the isomerisation of the Pd complexes in solution [4], the evidence favours a dissociative mechanism involving a solvento intermediate. The activation parameters given in the first two entries of Table 9 are consistent with this interpretation. In addition, on this basis, one would correctly predict a faster rate of isomerisation for SeCN with respect to SCN, since greater relief of steric strain would result from loss of the larger SeCN group to form the intermediate of lower co-ordination number [149].

Two mechanisms have been postulated for octahedral complexes. For the isomerisation of complexes containing *S*-bonded thiocyanate both intramolecular and ion-pair mechanisms have been suggested. Haim and Sutin [39] do not favour the former mechanism for the isomerisation of $(OH_2)_5CrSCN^{2+}$ because of the prohibitive amount of energy required to bend the linear thiocyanate group. These authors [39] prefer the ion-pair mechanism. For this process, the dissociation of the ion-pair, $(OH_2)_5Cr^{3+} \cdot SCN^-$, to $(OH_2)_5Cr^{3+}$ and SCN^- must be slow compared to the internal return of the ion-pair. When the isomerisation—aquation reaction of $(OH_2)_5CrSCN^{2+}$ was carried out in the presence of Cl^- the amount of $(OH_2)_5CrCl^{2+}$ found was less than expected from competition experiments [150]. This would be expected for the ion-pair mechanism.

Pertinent to this problem of mechanism are the results obtained for the isomerisation of $(NH_3)_5CoSCN^{2+}$ during acid and base hydrolysis [47]. The isomerisation reaction occurred with little exchange of SCN^- in the complex with $N^{14}CS^-$ [47] in the solvent. An intramolecular mechanism in which the thiocyanate ion rearranges so as to bond to the cobalt through the filled π molecular orbital over all three atoms of NCS^- was proposed. Questions on the energetics of such a reaction remain unanswered. A further study [53] of the base hydrolysis of *trans*-$[(en)_2NH_3CoSCN]^{2+}$ where some isomerisation (S→ N) is observed implies that this process occurs with Co—SCN bond rupture since some *trans*→ *cis* rearrangement was observed. Thus it appears that the ion-pair mechanism best explains these results, as well.

TABLE 9

Kinetic data for isomerisation

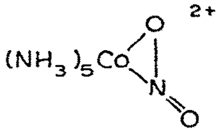
Complex	Solvent	k (s^{-1})(°C)	$\Delta H\neq$ (kcal mol^{-1})	$\Delta S\neq$ (eu)	Reference
$[Pd(Et_4dien)SeCN]^+$	DMF	3.1×10^{-4} (30°)	21.0	− 5	4
$[Pd(Et_4dien)SCN]^+$	DMF	1.93×10^{-4} (30°)	19.8	−10	4
$[Pd(Et_4dien)SeCN]^+$	DMF/H_2O (4/1)	1.1×10^{-4} (20°)			86
	Acetonitrile	0.76×10^{-4} (20°)			86
	Acetone	0.32×10^{-4} (20°)			86
$[Pd(Et_3dien)NCSe]^+$	Nujol	5×10^{-6} (40°)			68
$[Pd(Et_3dien)NCS]^+$	Nujol	3.6×10^{-6} (40°)			68
cis + *trans*-$(OH_2)_4Cr(NCS)(SCN)^+$	H_2O	8.3×10^{-5} (25°)	19.6	− 9.8	43
$Cr(OH_2)_5(NC)^{2+}$	H_2O	4.93×10^{-2} (25°)			89
$Cr(OH_2)_5(SCN)^{2+}$	H_2O	2.3×10^{-5} (25°)			39
$(NH_3)_5CoNH_2CHO^{3+}$	Nujol	1.8×10^{-4} (80°)			152
$Cr(OH_2)_5(SCN)^{2+} + Hg^{2+}$	H_2O	$5.4 \times 10^{2}\ M^{-1}\ s^{-1}$ (25°)			40
$(NH_3)_5CoSCN^{2+}$	H_2O	8×10^{-7} (25°)			47
$Fe_3[Cr(CN)_6]_2$ [a]	Solid	1.0×10^{-4} (50°)			91

[a] The overall isomerisation reaction involves four distinct structures in going from $[Fe^{2+}—N\equiv C—Cr^{3+}]$ to $[Cr^{3+}—N\equiv C—Fe^{2+}]$. The reaction studied involves the first step or half-isomerisation where the interstitial Fe^{2+} displaces Cr^{3+} from the carbon octahedra to give Fe^{2+} and Cr^{3+} in the carbon octahedra and Cr^{3+} in interstitial sites.

In a recent paper Melpolder and Burmeister [187] have described the synthesis of $(CN)_5CoSeCN^{3-}$ and compared its behaviour with that of the thiocyanato analogue. Isomerisation to the *N*-bonded forms apparently takes place by a dissociative mechanism in the solvents CH_2Cl_2, acetone, nitrobenzene and DMF. The possible formation of an ion—pair was also mentioned. In the solid state, data were presented on the effect of the countercation on the bonding mode of $(CN)_5CoSCN^{3-}$ [187].

The photochemically-induced isomerisation of $(NH_3)_5CoSCN^{2+}$ has been investigated [50] and is consistent with Co—SCN bond rupture. In solution $Co(NH_3)_5SCN^{2+}$ underwent a photoredox decomposition along with isomerisation upon irradiation of the first charge-transfer band at 333 nm. In the solid state, only isomerisation was observed. These results are consistent with a radical pair model [151] where separation of the radicals associated with the $(NH_3)_5Co$ and SCN led to the redox reaction whereas recombination resulted in isomerisation. In the case of isomerisation, the radical pair can be likened to the close ion-pair previously postulated but the SCN radical, by virtue of its reactivity, should be able to rotate easily thus being in a position to recombine with the $(NH_3)_5Co$ radical via the N atom. The fact that the Co—SCN linkage is bent in the ground state appears to make this rotation probable since $Co(NH_3)_5NCS^{2+}$ which has a linear Co—NCS linkage does not undergo photoisomerisation upon charge transfer excitation [151]. This isomer undergoes exclusively photoredox decomposition and aquation. Since only photoisomerisation occurs in the solid state, the implication is that the separation of the radical pair is finite but much smaller than in solution. This interpretation is consistent with the results obtained for the solid state isomerisation of $[(NH_3)_5CoSCN](SCN)_2$ [49], which has been shown to occur with incorporation of anionic thiocyanate. In addition, it was calculated that 45% of the isomerisation must occur by a dissociative path. Thus, it cannot be assumed that solid state isomerisations occur by an intramolecular process. In fact, there appears to be a parallel between the solid state and solution reactions.

In the case of the common nitrito→ nitro conversion, an intramolecular mechanism is generally favoured [113]. Recently [106], the photochemically-induced nitro→ nitrito isomerisation has led to the detection of a metastable transient which is thought to have the structure



Similar structures have been postulated in the solution isomerisation of $(NH_3)_5CoONO^{2+}$ [113] and $(CN)_5CoONO^{3-}$ [94]. The solid-state process involving $(NH_3)_5CoONO^{2+}$ was found to be an equilibrium process [103].

Equilibrium behaviour also has been investigated for nitro—nitrito systems

TABLE 10

Reduction studies of linkage isomers

Linkage isomers	Reductant	$k^{25°}$ (M^{-1} s^{-1})[a]	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)	Reference
$(NH_3)_5CoNCS^{2+}$	Cr^{2+}	19 (r)			141
$(NH_3)_5CoSCN^{2+}$	Cr^{2+}	1.9×10^5 (r) 0.8×10^5 (a)			141
$(NH_3)_5CoNCS^{2+}$	$Co(CN)_5^{3-}$	1.1×10^6 (r)			15, 142
$(NH_3)_5CoSCN^{2+}$	$Co(CN)_5^{3-}$	$>10^8$ $<2 \times 10^9$ (a)			143
$(OH_2)_5CrNCS^{2+}$	Cr^{2+}	1.4×10^{-4} (r)			153
$(OH_2)_5CrSCN^{2+}$	Cr^{2+}	40 (r)			38, 39
$(NH_3)_5CoNO_2^{2+}$	$Co(CN)_5^{3-}$	3.4×10^4 (r)			94
$(NH_3)_5CoONO^{2+}$	$Co(CN)_5^{3-}$	4.2×10^5 (r, N)[g]			154
$(NH_3)_5CoNH_2CHO^{3+}$ [b]	Cr^{2+}	1.74 (r)	12.0	−17	129
$(NH_3)_5CoOCHNH_2^{3+}$	Cr^{2+}	8.5×10^{-3} (O.S.)[c]	10.7	−32	129
$(NH_3)_5Co(N)py{-}4{\text -}CN^{3+}$	Cr^{2+}	124 (r)	0.2	−48	3
$(NH_3)_5CoNC{-}4{\text -}py(N)^{3+}$	Cr^{2+}	6370 (r)	0.3	−40	3
$(OH_2)_5CrNC{-}4{\text -}py(N)^{3+}$	Cr^{2+}	7100 (r)			3
$(OH_2)_5Cr(N)py{-}4{\text -}CN^{3+}$	Cr^{2+}	N.R.[d]			3
$(NH_3)_5CoNC{-}C_6H_4{-}4{\text -}CO_2^{2+}$ [e]	Cr^{2+}	~2			128
$(NH_3)_5CoO_2C{-}C_6H_4{-}4{\text -}CN^{2+}$	Cr^{2+}	0.18	7.5	−37	155
$(OH_2)_5CrNC^{2+}$	Cr^{2+}	1.60			89
$(OH_2)_5CrCN^{2+}$	Cr^{2+}	0.077	9.3	−32	148
$(NH_3)_5Co(N)py{-}4{\text -}CO_2^{2+}$ [f]	Cr^{2+}	~6			156
$(NH_3)_5CoO_2C{-}4{\text -}py(N)^{2+}$	Cr^{2+}	1.5×10^3			157

[a] r = remote attack, a = adjacent attack. [b] Only the conjugate base reacts. [c] O.S. = outer-sphere mechanism. [d] No reaction detectable. [e] The pK_a for 4-cyanobenzoic acid is 3.55 at $\mu = 0.01$ (Von G. Briegleb and A. Bieber, Z. Electrochem., 55 (1951) 250) and thus for the complex at $\mu = 1.0$ is estimated as 3.0 (R. Balahura, G. Wright and R. Jordan, J. Amer. Chem. Soc., 95 (1973) 1137). The rate is calculated from the slope of a plot of k_{obsd}(M^{-1} s^{-1}) versus $[H^+]^{-1}$ and the estimated K_a. [f] The reduction is assumed to take place by attack of reductant at the deprotonated carboxyl group. The rate is estimated from the reported (10) acid dependence of the reaction, 0.03 $[H^+]^{-1}$ M^{-1} s^{-1}, using the reported K_a of 0.0047 M. [g] Attack at remote N.

in non-aqueous solvents. For example, in chloroform, the dissolution of Ni(*N*,*N*-dimethylethylenediamine)$_2$(ONO)$_2$ and Ni(*N*,*N*′-diethylethylenediamine)$_2$(ONO)$_2$ results in a nitro—nitrito equilibrium mixture [31]. In fact, equilibrium mixtures of isomers is a very common observation, being reported as well for [Co(dimethylglyoximato)$_2$L(SCN)] (where L = pyridine or aniline) in many solvents [16], [Pd(AsPh$_3$)$_2$(SCN)$_2$] in DMF and DMSO [17] and for [Co(CN)$_5$SCN]$^{3-}$ with added tetra-n-butylammonium ion in H$_2$O [29]. Other examples are also known. The study of systems of this type by equilibrium methods such as T-jump and NMR should provide valuable kinetic data for interpretation of isomerisation reactions in solution.

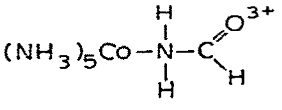
An interesting example of solid state isomerisation occurs with the (NH$_3$)$_5$Co^{3+} complex of *N*-bonded formamide. The complex [(NH$_3$)$_5$-CoNH$_2$CHO](ClO$_4$)$_3$ undergoes a transformation at room temperature over a period of months from a yellow-orange colour to pink-red. This latter material has been identified as the oxygen-bonded linkage isomer [(NH$_3$)$_5$-CoOCHNH$_2$][ClO$_4$)$_3$. Preliminary kinetic studies at 80°C indicate a rate constant of 1.8×10^{-4} s^{-1} [152].

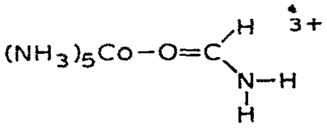
(ii) Redox reactions

The reduction of linkage isomers can provide information on the factors important in electron-transfer reactions. For inner-sphere reactions, the position of attack of the reductant and the electronic nature of the group or atom being attacked can often be distinguished using linkage isomers. The electron-mediating ability of the atoms involved and the orbitals used in transferring the electron can sometimes be ascertained as can the relative importance of precursor complex formation and the reducibility of the ligand. Results of this nature often lead to a more detailed electron transfer mechanism than would otherwise be obtained. These results may be illustrated with reference to selected examples contained in Table 10.

The reductions of (NH$_3$)$_5$CoNCS^{2+} and (NH$_3$)$_5$CoSCN^{2+} [141] indicate the importance of the stereochemistry of the ligand in its ability to bind to the reductant. The relative rates are indicative of the unusually high electron-mediating ability of co-ordinated sulphur (see mechanism p. 141).

The chromium(II) study of the linkage isomers of (NH$_3$)$_5$Co(formamide)$^{3+}$ [129], XXVIII and XXIX, delineates the necessary criteria for remote attack: (1) a donor atom in the bridging ligand must have a lone pair of electrons available for σ bonding


(XXVIII)


(XXIX)

to the incoming reductant and (2) the two donor atoms of the bridging ligand must be part of a conjugated system extending between the two metal centres. For isomer XXVIII the reductant attacks at the remote carbonyl oxygen (criterion(1)) and the electron transfer only takes place through the conjugate base (criterion (2)). In the case of isomer XXIX the remote NH_2 group cannot act as a bridge in electron transfer and an outer-sphere path was observed.

Reduction of linkage isomers containing large ligands, for example, $(NH_3)_5Co(4\text{-cyanopyridine})^{3+}$ may provide information on the transferring molecular orbitals as well as on the stability of the precursor complex. In the case of $(NH_3)_5Co(4\text{-cyanopyridine})^{3+}$ [3], the nitrile-bonded isomer is reduced fifty times faster than the isomer bonded through the pyridine nitrogen. Two factors have been suggested to account for this difference: (1) the precursor complex formed with the pyridine nitrogen is more stable than that formed with the nitrile nitrogen and (2) there is a larger concentration of the lowest empty antibonding molecular orbital on the pyridine nitrogen than on the nitrile nitrogen.

It appears that, in complexes containing remote carbonyl groups, the rate of electron transfer is controlled by the high energy of the lowest empty antibonding orbital of the COO^- group. For example the linkage isomers of $(NH_3)_5Co(4\text{-pyridinecarboxylate})^{2+}$ [156,157] are both reduced by remote attack. However, attack at the carboxyl group leads to an electron-transfer rate which is approximately 300 times slower than attack at the N atom in the linkage isomer. Since the hard Cr^{2+} would prefer to form a precursor complex with the hard carbonyl oxygen, one might expect this isomer to react faster than the one with a remote nitrogen atom. In fact, it was observed to react more slowly. The slower rate was attributed to the high energy of the electron-accepting antibonding orbital of the remote carboxyl group. This effect is also apparent in the comparison of electron transfer rates of other remote groups with COO^- [128].

Comparison of the reduction of linkage isomers of $(NH_3)_5Co(4\text{-cyanobenzoate})^{2+}$ [128] indicates the relative efficiency of electron mediation through co-ordinated and remote carboxyl groups. The rates shown in Table 10 reveal that remote attack is approximately ten times more efficient than adjacent attack in this case and may indicate a change in the detailed mechanism.

It is also expected that valuable information will be obtained from studies of the rates of intramolecular electron transfer employing linkage isomers although not much work has been done in this area to date [158—160].

G. CONCLUSIONS

The emphasis in the study of linkage isomers seems to be shifting from the novelty of their preparation to a serious study of their reactivities. However, much work remains to be done by the synthetic chemist as many potentially ambidentate ligands still defy preparation in linkage isomeric forms. Of fundamental importance to the understanding of the factors controlling this phenomenon are the kinetics of the isomerisation reactions themselves, which have not been studied in many cases, either in solution or in the solid state. Probably the most significant discovery in the past decade resulting from a study of linkage isomers has been the observation of equilibrium mixtures of isomers in various solvents. This should provide a unique opportunity to study the fundamental kinetic process of linkage isomerisation.

In the future, it seems likely that individual linkage isomers will be used as a sensitive mechanistic probe for redox reactions and may also be useful in a study of substitution processes. Linkage isomers containing large ligands as well as chelating groups where isomerisation between the two linkage isomeric forms is prevented, may prove to be the most suitable for these types of studies and probably will stimulate synthetic efforts in this direction.

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